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Supporting Information for:

Mobility of Lewis Acids within the Secondary Coordination Sphere: Toward a Model for Cooperative Substrate Binding

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General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an inert atmosphere drybox with an atmosphere of purified nitrogen. The drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as a −35 °C freezer for cooling samples and crystallizations. Solvents were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina. Solvents were then stored over sodium and/or molecular sieves. Benzene-d_6, THF-d_8, toluene-d_8, dichloromethane-d_2, and chloroform-*d* were purchased from Cambridge Isotope Laboratories. Benzene-d_6 was dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Chloroform-*d*, dichloromethane-d_2, and toluene-d_8 were distilled from CaH_2. THF-d_8 was dried over molecular sieves.

Zinc(II) bromide, NaOH, KOH, Na_2CO_3, NaI, tetrabutylammonium bromide, hydroquinone, NaH, iodobutane, 4-bromo-1-butene, 9-borabicyclo[3.3.1]nonane, potassium bis(trimethylsilylamide), diphenylammonium triflate, and thallium salts were purchased from commercial vendors and used as received. Anhydrous hydrazine was purchased from Sigma Aldrich, degassed, and passed through activated alumina prior to use. $^{H}NN^{tBu}$,[1] ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr_2$, and ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr_2(N_2H_4)$[2] were synthesized according to literature procedures.

NMR spectra were recorded on Varian Vnmrs 700 or Varian MR400 spectrometers. ^1H, ^{13}C, and ^{11}B chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane and referenced internally to the residual solvent peak. ^{11}B spectra were referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ^1H NMR spectrum. ^{11}B spectra are reported relative to $BF_3(OEt_2)$. Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q). Infrared spectra were recorded using a Nicolet iS10 FT-IR spectrometer. Samples were diluted into dry KBr and recorded as pellets.

Single crystals of ($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2$, ($^{vinyl}NN^{tBu}$)$ZnBr_2$, ($^{butenyl}NN^{tBu}$)$ZnBr_2$, ($^{4\text{-}BBN}NN^{tBu}$)$ZnBr_2$, [($^{4\text{-}BBN}NN^{tBu}$)$ZnBr(N_2H_4)$][PF_6], ($^{4\text{-}BBN}NN^{tBu}$)$ZnBr_2(N_2H_4)$, ($^{3\text{-}BPin}NN^{tBu}$)$ZnBr_2$, [($^{3\text{-}BBN}NN^{tBu}$)$ZnBr(N_2H_4)$][OTf], [$Zn(OPEt_3)_4$][PF_6]$_2$, ($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2(N_2H_4)$, ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr(N_2H_3)$, [($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2$]$_2(N_2H_4)$, ($^{butyl}NN^{tBu}$)$ZnBr_2$, and [($^{2\text{-}BBN}NN^{tBu}$)$ZnBr(N_2H_4)$][OTf] suitable for X-ray diffraction were coated with poly(isobutylene) oil and quickly transferred to the goniometer head of a Bruker AXS D8 Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator and a Photon100 CMOS area detector. Examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å). Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.[3] For all samples, the space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs[4] and refined by full matrix least squares against F^2 with all reflections using Shelxl2017 or Shelxl2018[5] using the graphical interface Shelxle.[6] If not specified otherwise, H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH_2, and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3, and 1.2 for CH_2, and C-H units, respectively. Additional data collection and refinement details, including description of disorder (where present) can be found in Tables S1-S12 and with the individual structure descriptions below the tables.

Synthesis of 2-(5-(*tert*-butyl)-1-(2-chloroethyl)-1*H*-pyrazol-3-yl)-6-methylpyridine (^{chloroethyl}NN^{tBu}). A 250 mL round bottom flask was charged with ^{H}NN^{tBu} (2-(5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-6-methylpyridine) (1.000 g, 4.645 mmol), NaOH (2.415 g, 60.380 mmol), Na_2CO_3 (1.959 g, 18.579 mmol), tetrabutylammonium bromide (0.030 g, 0.093 mmol) and 100 mL 1,2-dichloroethane. The mixture was heated at 50 °C for 20 hr with vigorous stirring. The flask was then cooled to room temperature and the solution was filtered over Celite. The solution was diluted with 50 mL H_2O and the organics were extracted with diethyl ether (3 x 50 mL), washed with water (3 x 50 mL), and dried over Na_2SO_4. Removal of volatiles afforded a viscous, brown oil. The material was purified by column chromatography on silica (R_f = 0.66; 3:1 hexane:ethyl acetate) and dried to afford a viscous yellow oil (0.456 g, 1.641 mmol, 35%) assigned as 2-(5-(*tert*-butyl)-1-(2-chloroethyl)-1*H*-pyrazol-3-yl)-6-methylpyridine (^{chloroethyl}NN^{tBu}). High-Res MS of $C_{15}H_{21}N_3Cl_1$ + H: Calc. 278.1424; Found 278.1417. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.44 (s, 9H, C(C*H*$_3$)$_3$), 2.61 (s, 3H, C*H*$_3$), 4.01 (t, *J* = 7.8, 2H, N-C*H*$_2$), 4.54 (t, *J* = 7.8, 2H, C*H*$_2$Cl), 6.65 (s, 1H, pyrazole-C*H*), 7.06 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.59 (t, *J* = 7.6, 1H, pyridine-C*H*), 7.68 (d, *J* = 7.6, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 24.71(*C*H$_3$), 30.18 (C(*C*H$_3$)$_3$), 31.36 (*C*(CH$_3$)$_3$), 41.80 (CH$_2$*C*H$_2$Cl), 52.06 (*C*H$_2$CH$_2$Cl), 102.29 (pyrazole-*C*H), 117.07, 121.90, 136.65 (*p*-pyridine-*C*H), 150.73, 151.80, 153.13, 158.13. Selected IR data (ATR, neat) υ = 2969, 1737, 1593, 1576, 1422, 1366, 1240, 1214, 923, 794 cm^{-1}.

Synthesis of 2-(5-(*tert*-butyl)-1-vinyl-1*H*-pyrazol-3-yl)-6-methylpyridine (^{vinyl}NN^{tBu}). A 250 mL round bottom flask was charged with ^{chloroethyl}NN^{tBu} (1.177 g, 4.237 mmol), KOH (5.942 g, 105.9 mmol), and hydroquinone (0.023 g, 0.212 mmol) in 100 mL of 2-isopropanol. A water condenser was attached to the flask and the solution was refluxed for 1 hr. The reaction was confirmed to have proceeded to completion by mass spectrometry and was cooled to room temperature. The solution was diluted with deionized water (50 mL) and neutralized by slow addition of a 5% HCl solution. The organic portion was extracted into diethyl ether (3 x 50 mL) and dried over Na_2SO_4. Removal of volatiles afforded a viscous, brown oil. The material was purified by column chromatography on silica(R_f = 0.50; 1:5 hexane:ethyl acetate) and dried to afford a fluffy white solid (1.022 g, 3.029 mmol, 72%) assigned as 2-(5-(*tert*-butyl)-1-vinyl-1*H*-pyrazol-3-yl)-6-methylpyridine (^{vinyl}NN^{tBu}). High-Res MS of $C_{15}H_{20}N_3$ + H: Calc. 242.1657; Found 242.1651. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.44 (s, 9H, C(C*H*$_3$)$_3$), 2.60 (s, 3H, C*H*$_3$), 4.90 (d, *J* = 8.6, 1H, C=CH*H*), 5.89 (d, *J* = 15.0, 1H, C=C*H*H), 6.78 (s, 1H, pyrazole-C*H*), 7.06 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.29 (dd, *J* = 15.0, 8.6, 1H, C*H*=CH$_2$), 7.60 (t, *J* = 7.6, 1H, pyridine-C*H*), 7.86 (d, *J* = 7.6, 1H, pyridine-C*H*). ^{1}H NMR (CH_2Cl_2, 25 °C) δ = 1.43 (s, 9H, C(C*H*$_3$)$_3$), 2.54 (s, 3H, C*H*$_3$), 4.87 (d, *J* = 8.7, 1H, C=CH*H*), 5.81 (d, *J* = 15.0, 1H, C=C*H*H), 6.72 (s, 1H, pyrazole-C*H*), 7.06 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.30 (dd, *J* = 15.0, 8.7, 1H, C*H*=CH$_2$), 7.60 (t, *J* = 7.6, 1H, pyridine-C*H*), 7.81 (d, *J* = 7.6, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 24.83 (*C*H$_3$), 30.33 (C(*C*H$_3$)$_3$), 31.58 (*C*(CH$_3$)$_3$), 102.14 (C=*C*H$_2$), 103.69 (pyrazole-*C*H), 117.46, 122.34, 131.90 (*C*=CH$_2$), 136 82 (*p*-pyridine-*C*H), 151.59, 151.73, 152.85, 158.18. Selected IR data (ATR, neat) υ = 2973, 2955, 1640, 1577, 1474, 1421, 1342, 1230, 882, 794 cm^{-1}.

Revised Synthesis of 2-(5-(*tert*-butyl)-1-butyl-1*H*-pyrazol-3-yl)-6-methylpyridine (^{butyl}NN^{tBu}) ligand. The preparation is analogous that the previous report except for reaction temperature.[3] Increasing the reaction temperature resulted in significantly improved yield. Inside a glovebox, a 500 mL Schlenk flask was charged with sodium hydride (0.600 g, 25.000 mmol) and 100 mL THF. The flask was removed from the glovebox and attached to a Schlenk line and chilled to -78 °C. While stirring and against positive N_2 flow, ^{H}NN^{tBu} (4.000 g, 18.579 mmol) was added. The flask was resealed with a septum containing a gas outlet. The reaction was slowly warmed to room temperature and stirred until all gas evolution subsided. With stirring, 1-iodobutane (13.600 g, 73.905 mmol) was added against a positive flow of N_2. A reflux condenser containing a gas outlet was attached and the flask was refluxed for 20 hr. The light yellow solution was cooled to room temperature and volatiles were removed in vacuo. The material was dissolved in 100 mL chloroform and filtered through Celite and concentrated to a deep orange solid. The material was purified by column chromatography on silica (R_f = 0.57; 2:1 hexane:ethyl acetate), and dried to afford white powder (3.868 g, 14.251 mmol, 77%) identified as ^{butyl}NN^{tBu}.

Synthesis of 2-(1-(but-3-en-1-yl)-5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-6-methylpyridine (^{butenyl}NN^{tBu}). Inside a glovebox, a 500 mL Schlenk flask was charged with sodium hydride (0.355 g, 14.792 mmol) and 100 mL THF. The flask was removed from the glovebox and attached to a Schlenk line and chilled to -78 °C. While stirring and against positive N_2 flow, ^{H}NN^{tBu} (2.440 g, 11.333 mmol) was added. The flask was resealed with a septum containing a gas outlet. The reaction was slowly warmed to room temperature and stirred until all gas evolution subsided. With stirring, 4-bromo-1-butene (6.120 g, 45.333 mmol) was added against a positive flow of N_2. A reflux condenser containing a gas outlet was attached and the flask was refluxed for 16 hr. The light yellow solution was cooled to room temperature and volatiles were removed in vacuo. The material was dissolved in 100 mL chloroform and filtered through Celite and concentrated to a deep orange solid. The material was purified by column chromatography on silica (R_f = 0.54; 2:1 hexane:ethyl acetate), and dried to afford white powder (0.265 g, 0.983 mmol, 9%) assigned as ^{butenyl}NN^{tBu}. High-Res MS of $C_{17}H_{23}N_3$ + H: Calc. 270.1970; Found 270.2269. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.43 (s, 9H, C(C*H*$_3$)$_3$), 2.60 (s, 3H, C*H*$_3$), 2.75 (q, *J* = 8.0, 2H, C*H*$_2$) 4.28 (t, *J* = 8.0, 2H, NC*H*$_2$), 5.09 (d, *J* = 10.2, 1H, C=C*H*H), 5.16 (d, *J* = 17.1, 1H, C=C*H*H), 5.87 (m, 1H, C*H*=CH$_2$), 6.63 (s, 1H, pyrazole-C*H*), 7.03 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.58 (t, *J* = 7.6, 1H, *p*-pyridine-C*H*), 7.71 (d, *J* = 7.6, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 24.88 (*C*H$_3$), 30.35 (C(*C*H$_3$)$_3$), 31.52 (*C*(CH$_3$)$_3$), 35.30 (*C*H$_2$), 50.70 (N-*C*H$_2$), 102.02 (pyrazole-*C*H), 117.11, 121.75, 134.66 (*C*=CH$_2$), 136.73 (*p*-pyridine-*C*H), 150.21, 152.36, 152.62, 158.16. Selected IR data (ATR, neat) υ = 1593, 1574, 1476, 1424, 1369, 1248, 913, 797 cm^{-1}.

Synthesis of (^{vinyl}NN^{tBu})ZnBr$_2$. A 20 mL scintillation vial was charged with ^{vinyl}NN^{tBu} (0.181 g, 0.750 mmol), $ZnBr_2$ (0.169 g, 0.750 mmol), and 15 mL DCM. The reaction was stirred 18 hrs at room temperature then filtered. The volatiles were then removed in vacuo and the product was washed with 15 mL pentane to afford white powder (0.187 g, 0.401 mmol, 53%) assigned by NMR as (^{vinyl}NN^{tBu})$ZnBr_2$. Single, X-ray quality crystals were obtained by diffusion *n*-pentane into a THF solution of (^{vinyl}NN^{tBu})$ZnBr_2$ at room temperature. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.48 (s, 9H, C(C*H*$_3$)$_3$), 2.97 (s, 3H, C*H*$_3$), 5.56 (dd, *J* = 8.7, 2.7, 1H, C=CH*H*), 6.59 (dd, *J* = 15.3, 2.6, 1H, C=C*H*H), 6.69 (s, 1H, pyrazole-C*H*), 7.27 (dd, *J* = 15.3, 8.7, 1H, C*H*=CH$_2$), 7.40 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.65 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.94 (t, *J* = 7.8, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 24.46 (*C*H$_3$), 29.66 (C(*C*H$_3$)$_3$), 32.27 (*C*(CH$_3$)$_3$), 102.88, 113.69, 118.50, 126.45, 130.66, 141.03,

146.05, 147.00, 156.92, 159.98. Selected IR data (ATR, neat) υ = 2974, 1639, 1610, 1570, 1342, 1242, 1162, 1096, 1022, 894, 807, 727 cm^{-1}.

Attempted hydroboration of (^{vinyl}NN^{tBu})ZnBr$_2$ to form ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$. A 20 mL scintillation vial was charged with (^{vinyl}NN^{tBu})ZnBr$_2$ (0.025 g, 0.054 mmol), 9-borabicyclo[3.3.1]nonane (0.012 g, 0.097 mmol), and 3 mL THF. Upon dissolution, three separate J-Young NMR tubes were each charged with 1 mL of the reaction solution. The tubes were heated at 45, 65, and 85 °C for 16 hr and investigated by ^{1}H NMR. Spectra can be found below. In none of the cases were resonances consistent with ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$ observed. Observations: 45 °C – primarily (^{vinyl}NN^{tBu})ZnBr$_2$ with trace formation of a broad, unidentified product; 65 °C – increasing quantity of the broad, unidentified product; 85 °C – minimal (^{vinyl}NN^{tBu})ZnBr$_2$ remains with multiple, unidentified species.

Synthesis of ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$. A 20 mL scintillation vial was charged with ^{vinyl}NN^{tBu} (0.566 g, 2.347 mmol), 9-borabicyclo[3.3.1]nonane (0.430 g, 3.521 mmol), and 15 mL dichloromethane. The reaction was stirred for 16 hr at room temperature. This solution was transferred to a new 20 mL scintillation vial charged with zinc bromide (0.555 g, 2.464 mmol, crushed into a fine powder). The reaction was stirred an additional 72 hr at room temperature, and dried. The material was dissolved in benzene, filtered, and dried to afford white powder (0.838 g, 1.447 mmol, 62%) assigned as ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$. Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a C_6H_6 solution of ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$ at room temperature. MALDI-TOF of $C_{23}H_{34}N_3Br_2B_1Zn_1$ - Br: Calc. 506.132; Found 505.562. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.32 (s, 2H, B-C*H*), 1.48 (s, 9H, C(C*H*$_3$)$_3$), 1.84-1.93 (m, 12H, BBN-C*H*), 2.49 (t, *J* = 8.9, 2H, B-C*H*$_2$), 2.94 (s, 3H, C*H*$_3$), 4.72 (t, *J* = 8.9, 2H, N-C*H*$_2$), 6.56 (s, 1H, pyrazole-C*H*), 7.35 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.60 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.90 (t, *J* = 7.8, 1H, pyridine-C*H*). ^{1}H NMR (CH_2Cl_2, 25 °C) δ = 1.30 (s, 2H, B-C*H*), 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.80-1.93 (m, 12H, BBN-C*H*), 2.45 (t, *J* = 8.8, 2H, B-C*H*$_2$), 2.87 (s, 3H, C*H*$_3$), 4.69 (t, *J* = 8.8, 2H, N-C*H*$_2$), 6.63 (s, 1H, pyrazole-C*H*), 7.36 (d, *J* = 7.7, 1H, pyridine-C*H*), 7.64 (d, *J* = 7.7, 1H, pyridine-C*H*), 7.93 (t, *J* = 7.7, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 23.31 (BBN-*C*H$_2$), 24.51 (*C*H$_3$), 30.15 (C(*C*H$_3$)$_3$), 31.43 (B-*C*H), 32.21 (*C*(CH$_3$)$_3$), 33.28 (BBN-*C*H$_2$), 33.36 (B-*C*H$_2$), 50.33 (N-*C*H$_2$), 101.58, 117.96, 125.67, 140.94, 145.48, 146.71, 156.56, 159.67. Selected IR data (ATR, neat) υ = 1613, 1482, 1325, 1247, 1160, 1100, 1021, 803 cm^{-1}.

Synthesis of (^{butenyl}NN^{tBu})ZnBr$_2$. A 20 mL scintillation vial was charged with zinc bromide (0.155 g, 0.688 mmol), ^{butenyl}NN^{tBu} (0.181 g, 0.672 mmol), and 10 mL dichloromethane. The reaction was stirred for 40 hr at room temperature, filtered, and dried. The material was washed with 2 x 10 mL *n*-pentane and dried to afford white powder (0.299 g, 0.605 mmol, 90%) assigned as (^{butenyl}NN^{tBu})ZnBr$_2$. Single, X-ray quality crystals were obtained by diffusing diethyl ether into a tetrahydrofuran solution of (^{butenyl}NN^{tBu})ZnBr$_2$ at room temperature. High-Res MS of $C_{17}H_{23}N_3Br_2Zn_1$ - Br: Calc. 412.0367; Found 412.0362. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.47 (s, 9H, C(C*H*$_3$)$_3$), 2.94 (s, 3H, C*H*$_3$), 3.01 (q, *J* = 8.3, 2H, N-CH$_2$C*H*$_2$), 4.48 (t, *J* = 8.3, 2H, N-C*H*$_2$), 5.18 (d, *J* = 10.2, 1H, C=CH*H*), 5.33 (d, *J* = 17.0, 1H, C=C*H*H), 5.88 (m, 1H, C*H*=CH$_2$), 6.58 (s, 1H, pyrazole C-*H*), 7.37 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.62 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.92 (t, *J* = 7.8, 1H, *p*-pyridine C-*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 24.54, 30.12 (C(*C*H$_3$)$_3$), 32.24 (*C*(CH$_3$)$_3$), 34.97, 52.48 (N-*C*H$_2$), 101.91 (pyrazole *C*-H), 118.22, 118.96, 125.92 (pyridine *C*-H), 132.66, 141.11 (*p*-pyridine *C*-H), 145.93, 146.49, 157.19, 159.67. Selected IR data (ATR, neat) υ = 1611, 1481, 1372, 924 cm^{-1}.

Synthesis of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$. A 20 mL scintillation vial was charged with ($^{\text{butenyl}}$NN$^{t\text{Bu}}$)ZnBr$_2$ (0.281 g, 0.568 mmol), 9-borabicyclo[3.3.1]nonane (0.104 g, 0.852 mmol), and 10 mL tetrahydrofuran. The vial was stirred for 18 hr, volatiles were removed in vacuo, and the resulting material washed with 2 x 15 mL *n*-pentane to afford white powder (0.313 g, 0.508 mmol, 89%) assigned as ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$. Single, X-ray quality crystals were obtained by diffusing *n*-hexane into a benzene solution of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ at room temperature. MALDI-TOF of $C_{25}H_{38}N_3B_1Br_2Zn_1$ - Br: Calc. 534.163; Found 533.662. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.22 (m, 2H, B-CH_2), 1.47 (s, 9H, C(CH_3)$_3$), 1.54 (m, 2H, B-C*H*), 1.69 (m, 4H, BBN-C*H*), 1.73 (m, 2H, CH_2CH$_2$B), 1.84 (m, 8H, BBN-C*H*), 2.30 (m, 2H, N-CH$_2$CH_2), 2.94 (s, 3H, CH_3), 4.44 (t, *J* = 7.0, 2H, N-CH_2), 6.57 (s, 1H, pyrazole C-*H*), 7.35 (d, *J* = 7.0, 1H, pyridine C-*H*), 7.61 (d, *J* = 7.0, 1H, pyridine C-*H*), 7.90 (t, *J* = 7.0, 1H, *p*-pyridine C-*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 22.01, 23.33, 24.51, 27.43 (B-*C*H$_2$), 30.08 (C(*C*H$_3$)$_3$), 31.10 (B-*C*H), 32.22 (*C*(CH$_3$)$_3$), 33.27 (BBN-*C*H$_2$), 33.81, 52.71 (N-*C*H$_2$), 101.72 (pyrazole *C*-H), 118.08, 118.96, 125.77 (pyridine *C*-H), 141.02 (*p*-pyridine *C*-H), 145.67, 146.59, 156.85, 159.63. ^{11}B NMR ($CDCl_3$, 25 °C) δ = 87.78. Selected IR data (KBr) υ = 3128, 1610, 1481, 1370, 1022, 808 cm^{-1}.

Synthesis of ($^{\text{butyl}}$NN$^{t\text{Bu}}$)ZnBr$_2$. A 20 mL scintillation vial was charged with zinc bromide (0.835 g, 3.707 mmol), $^{\text{butyl}}$NN$^{t\text{Bu}}$ (1.000 g, 3.684 mmol), and 20 mL dichloromethane. The reaction was stirred for 40 hr at room temperature, filtered, and dried. The material was washed with 2 x 20 mL *n*-pentane and dried to afford white powder (1.776 g, 3.576 mmol, 97%) assigned as ($^{\text{butyl}}$NN$^{t\text{Bu}}$)ZnBr$_2$. Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a dichloromethane solution of ($^{\text{butyl}}$NN$^{t\text{Bu}}$)ZnBr$_2$ at room temperature. High-Res MS of $C_{17}H_{25}N_3Br_2Zn_1$ - Br: Calc. 414.0523; Found 414.0679. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.07 (t, *J* = 7.4, 3H, CH$_2$CH_3), 1.46 (s, 9H, C(CH_3)$_3$), 1.53 (h, *J* = 7.4, 2H), 2.24 (m, 2H, CH$_2$CH_2CH$_2$), 2.94 (s, 3H, CH_3), 4.41 (t, *J* = 8.5, 2H, N-CH_2), 6.56 (s, 1H, pyrazole C-*H*), 7.35 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.60 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.90 (t, *J* = 7.8, 1H, *p*-pyridine C-*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 13.70 (*C*H$_3$), 20.20, 24.51, 30.06 (C(*C*H$_3$)$_3$), 32.20 (*C*(CH$_3$)$_3$), 32.79 (CH$_2$*C*H$_2$CH$_2$), 52.48 (N-*C*H$_2$), 101.68 (pyrazole *C*-H), 118.07 (pyridine *C*-H), 125.78 (pyridine *C*-H), 141.01 (*p*-pyridine *C*-H), 145.68, 146.57, 156.88, 159.64. Selected IR data (ATR, neat) υ = 3131, 1609, 1471, 1369, 1021, 808 cm^{-1}.

Synthesis of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$). A 20 mL scintillation vial was charged with ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ (0.973 g, 1.653 mmol) and 15 mL THF. While stirring, N_2H_4 (0.060 mL, 1.912 mmol) was added and the reaction was stirred at room temperature for 24 hours. The mixture was filtered and volatiles were removed in vacuo. The material was washed with *n*-pentane (2 x 10 mL) and dried to afford a white powder (0.590 g, 0.950 mmol, 58%) assigned as ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$). Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a C_6H_6 solution of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$) at room temperature. MALDI-TOF of $C_{23}H_{38}N_5Br_2B_1Zn_1$ - HBr: Calc. 537.162; Found 535.559. For $C_{23}H_{38}N_5Br_2Zn_1$ – (HBr + N_2H_3): Calc. 506.132; Found 505.561. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 0.73 (s, broad, 2H, B-CH_2), 1.44 (m, 2H, B-CH_2), 1.48 (s, 9H, C(CH_3)$_3$), 1.57 (m, 2H, BBN-C*H*), 1.68-1.79 (m, 8H, BBN-C*H*), 1.90 (m, 2H, BBN-C*H*), 2.92 (s, 3H, CH_3), 4.51 (m, 2H, N-CH_2), 6.53 (s, 1H, pyrazole-C*H*), 7.34 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.60 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.91 (t, *J* = 7.8, 1H, pyridine-C*H*). ^{1}H NMR (THF, 25 °C, some resonances are overlapping with OC_4H_8 resonances) δ = 0.64 (s, broad, 2H, B-C*H*), 1.36 (m, 2H, B-CH_2), 1.46 (s, 9H, C(CH_3)$_3$), 2.83 (s, 3H, CH_3), 4.48 (m, 2H, N-CH_2), 5.96 (t, *J* = 5.1, 2H, NH_2NH$_2$), 6.82 (s, 1H, pyrazole-C*H*), 7.41 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.83 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.97 (t, *J* = 7.6, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 21.34 (broad), 21.52 (broad), 24.40 (broad), 24.57 (*C*H$_3$), 30.05 (C(*C*H$_3$)$_3$), 31.44 (broad), 32.18 (*C*(CH$_3$)$_3$), 52.87 (N-*C*H$_2$),

101.33, 117.97, 125.49, 141.16, 144.87, 146.99, 157.00, 159.40. Selected IR data (KBr) υ = 3354 (N-H), 3336 (N-H), 3320 (NH), 3281 (N-H), 3246 (N-H), 3224 (N-H), 3161 (N-H), 1610, 1482, 1320, 796 cm^{-1}.

Synthesis of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$]$_2$(N$_2$H$_4$). A 20 mL scintillation vial was charged with ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ (0.095 g, 0.161 mmol) and 10 mL THF. While stirring, N_2H_4 (0.159 M stock solution in THF, 0.508 mL, 0.081 mmol) was added and the reaction was stirred at room temperature for 20 hours. The mixture was filtered and volatiles were removed in vacuo. The material was washed with *n*-pentane (2 x 10 mL) and dried to quantitatively afford a white powder assigned as [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$]$_2$(N$_2$H$_4$). Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a THF solution of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$]$_2$(N$_2$H$_4$) at room temperature. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 1.17 (s, broad, 2H, B-C*H*), 1.48 (s, 9H, C(CH_3)$_3$), 1.54 (m, 2H, B-CH_2), 1.78-1.87 (m, 10H, BBN-C*H*), 1.91 (m, 2H, BBN-C*H*), 2.92 (s, 3H, CH_3), 4.56 (t, *J* = 9.5, 2H, N-CH_2), 5.51 (broad, 2H, NH_2NH$_2$), 6.53 (s, 1H, pyrazole-C*H*), 7.33 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.59 (d, *J* = 7.8, 1H, pyridine-C*H*), 7.90 (t, *J* = 7.8, 1H, pyridine-C*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 22.87 (broad), 23.49 (broad), 24.03, 24.65, 30.13 (C(*C*H$_3$)$_3$), 31.75 (broad), 32.16 (*C*(CH$_3$)$_3$), 51.89 (N-*C*H$_2$), 101.37, 117.95, 125.50, 141.10, 144.94, 146.99, 157.10, 159.51. Selected IR data (KBr) υ = 3259 (N-H), 3202 (N-H), 3155 (N-H), 3101 (N-H), 1611, 1574, 1372, 1316, 1247, 795 cm^{-1}.

Synthesis of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$). A 20 mL scintillation vial was charged with ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ (0.638 g, 1.035 mmol) and 12 mL THF. A separate vial was charged with N_2H_4 (0.0324 mL, 1.032 mmol) and 1 mL THF. While stirring, the solution of N_2H_4 was added dropwise to the vial containing ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ and stirred for 15 min. Volatiles were removed in vacuo and the resulting material washed with *n*-pentane (2 x 10 mL) to afford white powder (0.634 g, 0.977 mmol, 94%) assigned as ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$). Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a benzene solution of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$) at room temperature. ^{1}H NMR ($CDCl_3$, 25 °C) δ = 0.61 (t, *J* = 8.2, 2H, B-CH_2), 0.68 (s, 2H, B-C*H*), 1.41 (m, 2H, BCH$_2$CH_2), 1.47 (s, 9H, C(CH_3)$_3$), 1.50 (m, 2H, BBN-C*H*), 1.61-1.70 (m, 8H, BBN-C*H*), 1.83 (m, 4H, BBN-C*H*), 2.21 (m, 2H, N-CH$_2$CH_2), 2.93 (s, 3H, CH_3), 4.49 (t, *J* = 8.1, 2H, N-CH_2), 4.52 (broad, 4H, N$_2$H$_4$), 6.56 (s, 1H, pyrazole C-*H*), 7.35 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.61 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.91 (t, *J* = 7.8, 1H, *p*-pyridine C-*H*). ^{13}C NMR ($CDCl_3$, 25 °C) δ = 18.22 (B-*C*H$_2$), 22.29 (B-*C*H), 23.50, 24.54, 24.80 (BBN-C*H*), 30.08 (C(*C*H$_3$)$_3$), 31.58 (BBN-*C*H$_2$), 32.28 (*C*(CH$_3$)$_3$), 35.17, 53.69 (N-*C*H$_2$), 101.68 (pyrazole *C*-H), 118.11, 125.74 (pyridine *C*-H), 141.11 (*p*-pyridine *C*-H), 145.45, 146.68, 157.09, 159.57. ^{11}B NMR (THF, 25 °C) δ = -4.62. Selected IR data (KBr) υ = 3355 (N-H), 3304 (N-H), 3167 (N-H), 3128 (N-H), 3068 (N-H), 1610, 1534, 1050, 900 cm^{-1}.

Synthesis of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]. The following is for preparation of the hexafluorophosphate salt. The trifluoromethanesulfonate salt was prepared analogously. This preparation describes a one-pot method. Alternately, ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) can be treated directly with a thallium(I) salt. A 20 mL scintillation vial was charged with ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2 (0.150 g, 0.255 mmol) and 2 mL THF. While stirring, hydrazine (0.159 M stock solution in THF; 0.254 mmol) was added and the solution stirred for 5 min. Volatiles were removed in vacuo. The material was redissolved in 8 mL DCM/THF (50:50) and thallium hexafluorophosphate (0.089 g, 0.255 mmol) was added. The reaction was stirred 30 min, filtered, and dried. The material was twice precipitated from minimal dichloromethane with *n*-pentane and dried to afford white powder (0.142 g, 0.207 mmol, 81%) assigned as [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]. Single, X-ray quality crystals of the trifluoromethanesulfonate salt were obtained by diffusing *n*-pentane into a THF solution of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] at room temperature. MALDI-TOF of $C_{23}H_{38}N_5Br_1B_1Zn_1(SO_3CF_3)$ - HSO_3CF_3: Calc. 537.162; Found 535.607. Sample – (HSO_3CF_3 + N_2H_3): Calc. 506.132; Found 505.608. (NMR data for PF_6 salt) ^{1}H NMR (THF-D_8, 25 °C) δ = 0.69 (s, 2H, B-C*H*), 1.50 (s, 9H, C(CH_3)$_3$), 1.56 (m, 4H, BBN-C*H*), 1.73 (m, 8H, BBN-CH_2), 1.87 (m, 2H, B-CH_2), 2.82 (s, 3H, CH_3), 4.52 (t, *J* = 6.6, 2H, N-CH_2), 5.91 (s, broad, 4H, N_2H_4), 7.08 (s, 1H, pyrazole-C*H*), 7.56 (d, *J* = 7.6, 1H, pyridine-C*H*), 7.98 (d, *J* = 7.6, 1H, pyridine-C*H*), 8.11 (t, *J* = 7.6, 1H, pyridine-C*H*). ^{1}H NMR ($CDCl_3$, 25 °C) δ = 0.56 (s, 2H, B-CH_2), 1.51 (s, 9H, C(CH_3)), 1.58 (m, 4H, BBN-CH), 1.73 (m, 4H, BBN-C*H*), 1.76 (m, 4H, BBN-C*H*), 1.85 (m, 2H, B-CH_2), 2.86 (s, 3H, CH_3), 4.37 (s, broad, 2H, N-C*H*H), 4.60 (m, 2H, N-CH*H*; overlapping with broad NH_2 resonance), 6.10 (broad, 2H, Zn-NH_2), 6.78 (s, 1H, pyrazole-C*H*), 7.48 (d, *J* = 6.2, 1H, pyridine-C*H*), 7.71 (d, *J* = 6.2, 1H, pyridine-C*H*), 8.03 (t, *J* = 6.2, 1H, pyridine-C*H*). ^{1}H NMR ($CDCl_3$, -50 °C) δ = 0.31 (s, 1H, B-C*H*), 0.64 (s, 1H, B-C*H*), 1.15-1.34 (m, 4H, BBN-C*H*), 1.48 (s, 9H, C(CH_3)$_3$), 1.54-1.64 (m, 2 x 1H, B-C*H*H and B-CH*H*), 1.64-1.89 (m, 8H, BBN-C*H*), 2.82 (s, 3H, CH_3), 4.34 (d, *J* = 10.7, 1H, NC*H*H), 4.51 (m, 1H, B-N*H*H), 4.54 (m, 1H, NCH*H*), 4.65 (t, *J* = 7.3, 1H, B-NH*H*), 6.06 (s, broad, 1H, Zn-N*H*H), 6.39 (s, broad, 1H, Zn-NH*H*), 6.80 (s, 1H, pyrazole-CH), 7.51 (d, *J* = 7.4, 1H, pyridine-C*H*), 7.71 (d, *J* = 7.4, 1H, pyridine-C*H*), 8.07 (t, *J* = 7.6, 1H, pyridine-C*H*). Due to low solubility and the dynamic nature of the compound, high resolution ^{13}C NMR were challenging to obtain. The following are select resonances associated with the molecule: ^{13}C NMR (CD_2Cl_2, 25 °C) δ = 18.18, 21.93, 29.60, 30.62, 32.93, 51.80, 103.52, 118.97, 126.73, 142.09, 147.28, 160.02. Selected IR data for X = OTf (KBr) υ = 3247 (N-H), 3211 (N-H), 3157 (N-H), 3106 (N-H), 1614, 1483, 1029, 796, 632 cm^{-1}.

Synthesis of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]. A 20 mL scintillation vial was charged with ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$ (0.131 g, 0.206 mmol) and 8 mL THF. While stirring, thallium(I) trifluoromethanesulfonate (0.072 g, 0.204 mmol) was added resulting is rapid formation of a colorless precipitate. After 20 min, the solution was filtered and dried. The colorless material was washed with 2 x 10 mL *n*-pentane and dried to afford white powder (0.129 g, 0.183 mmol, 89%) assigned as [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]. Single, X-ray quality crystals were obtained by two methods: 1) layering a THF solution of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] with hexamethyldisiloxane at room temperature, or 2) diffusing diethyl ether into a dichloromethane solution of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] at room temperature. MALDI-TOF of $C_{24}H_{40}N_5Br_1B_1Zn_1(SO_3CF_3)$ - HSO_3CF_3: Calc. 551.177; Found 549.692. Sample – (HSO_3CF_3 + N_2H_3): Calc. 520.147; Found 519.710. ^{1}H NMR (THF, 25 °C) δ = 0.40 (s, broad, 2H, B-CH_2 or B-C*H*), 0.60 (s, broad, 1H, B-CH_2 or B-C*H*), 1.47 (s, 9H, C(CH_3)$_3$), 2.82 (s, 3H, CH_3), 4.44 (t, *J* = 6.4, 2H, N-CH_2), 5.60 (broad, 2H, NH_2NH$_2$), 6.29 (broad, 2H, NH$_2$NH_2), 7.00 (s, 1H, pyrazole C-*H*), 7.52 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.93 (d, *J* = 7.8, 1H, pyridine C-*H*), 8.06 (t, *J* = 7.8, 1H, *p*-pyridine C-*H*). ^{1}H NMR ($CDCl_3$, 25 °C) δ = 0.61 (s, broad, 2H, B-CH_2 or B-C*H*), 0.73 (s, broad, 1H, B-CH_2 or B-C*H*), 1.49 (s, 9H, C(CH_3)$_3$), 1.63 (m, 8H, BBN-C*H*), 1.69 (m, 4H, BBN-C*H*), 2.10 (m, 2H, CH$_2$CH_2CH$_2$), 2.87 (s, 3H, CH_3), 4.40 (t, *J* = 7.4, 2H, N-CH_2), 5.13 (broad, 4H, N_2H_4), 6.64 (s, 1H, pyrazole C-*H*), 7.41 (d, *J* = 6.9, 1H, pyridine C-*H*), 7.65 (d, *J* = 6.9, 1H, pyridine C-*H*), 7.97 (t, *J* = 6.9, 1H, *p*-pyridine C-*H*). ^{1}H NMR (CD_2Cl_2, -60 °C) δ = -0.26 (t, *J* = 14.5, 1H, B-C*H*H), 0.37 (s, 1H, B-C*H*), 0.60 (s, 1H, B-C*H*), 0.67 (t, *J* = 14.5, B-CH*H*), 1.38 (m, 2H, BBN-C*H*), 1.43 (s, 9H, C(CH_3)$_3$), 1.54 (m, 6H, BBN-C*H*), 1.68 (m, 4H, BBN-C*H*), 2.01 (m, 1H, CH$_2$C*H*HCH$_2$), 2.28 (m, 1H, CH$_2$CH*H*CH$_2$), 2.76 (s, 3H, CH_3), 4.27 (d, *J* = 11.3, N-C*H*H), 4.49 (t, *J* = 10.2, N-CH*H*), 4.55 (s, broad, 1H, B-N*H*H), 5.46 (s, broad, 1H, B-NH*H*), 5.52 (s, 1H, Zn-N*H*H), 6.22 (s, 1H, Zn-NH*H*), 6.78 (s, 1H, pyrazole C-*H*), 7.43 (d, *J* = 7.8, 1H, pyridine C-*H*), 7.73 (d, *J* = 7.8, 1H, pyridine C-*H*), 8.04 (t, *J* = 7.8, 1H, *p*-pyridine C-*H*). Due to low solubility and the dynamic nature of the compound, high resolution ^{13}C NMR were challenging to obtain. The following are select resonances associated with the molecule: ^{13}C NMR ($CDCl_3$, 25 °C) δ = 15.41, 22.92, 24.48, 29.78, 31.60, 32.23, 55.08, 102.16, 118.52, 118.82, 120.63, 126.38, 141.86, 146.55, 158.60, 159.99. Selected IR data (KBr) υ = 3224, 3146, 2975, 2922, 2870, 2840, 1615, 1577, 1484, 1028, 799, 638 cm^{-1}.

Synthesis of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]. The following describes the synthesis of the trifluoromethanesulfonate salt directly from ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4). We also provide a one-pot method for the synthesis of the hexafluorophosphate salt. **[($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]**: A 20 mL scintillation vial was charged with ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) (0.096 g, 0.148 mmol), and 5 mL THF. While stirring, thallium(I) trifluoromethanesulfonate (0.052 g, 0.148 mmol) was added resulting in rapid formation of a white precipitate. After 20 min stirring at room temperature, the solution was filtered and dried. The colorless material was washed with 2 x 10 mL *n*-pentane and dried to afford white powder (0.110 g, 0.127 mmol, 86%) assigned as [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]. MALDI-TOF of $C_{25}H_{42}N_5Br_1B_1Zn_1(SO_3CF_3)$ - HSO_3CF_3: Calc. 565.193; Found 563.694. Sample – (HSO_3CF_3 + N_2H_3): Calc. 534.163; Found 533.691. **[($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]**: A 20 mL scintillation vial was charged with ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2 (0.150 g, 0.243 mmol) and 2 mL THF. While stirring, hydrazine (0.159 M stock solution in THF; 0.253 mmol) was added and the solution stirred for 5 min. Volatiles were removed in vacuo. The material was redissolved in 8 mL DCM/THF (50:50) and thallium hexafluorophosphate (0.085 g, 0.243 mmol) was added. The reaction was stirred 30 min, filtered, and dried. The material was twice precipitated from minimal dichloromethane with *n*-pentane and dried to afford white powder (0.151 g, 0.212 mmol, 87%) assigned as [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]. Single, X-ray quality crystals of the trifluoromethanesulfonate salt were obtained by diffusing *n*-pentane into a dichloromethane solution of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] at room temperature. ^{1}H NMR (CD_2Cl_2, 25 °C) δ = 0.66 (s, broad, 2H, B-CH_2), 0.81 (s, broad, 2H, B-C*H*), 1.63 (s, 9H, C(CH_3)$_3$), 1.54 (m, 2H, B-CH$_2$CH_2), 1.63 (m, 8H, BBN-C*H*), 1.71 (m, 4H, BBN-C*H*), 1.86 (m, 2H, N-CH$_2$CH_2), 2.83 (s, 3H, CH_3), 4.64 (s, broad, 2H, N-CH_2), 5.55 (s, broad, 4H, N_2H_4), 6.81 (s, 1H, pyrazole-C*H*), 7.52 (d, *J* = 7.7, 1H, pyridine-C*H*), 7.75 (d, *J* = 7.7, 1H, pyridine-C*H*), 8.07 (t, *J* = 7.7, 1H, pyridine-C*H*). ^{1}H NMR (CD_2Cl_2, -75 °C) δ = 0.45 (s, 1H, B-C*H*), 0.56 (m, 2H, B-CH_2), 0.62 (s, 1H, B-C*H*), 1.41 (s, 9H, C(CH_3)$_3$), 1.58 (m, 8H, BBN-C*H*), 1.63 (m, 2H, B-CH$_2$CH_2), 1.75 (m, 2H, BBN-C*H*), 1.81 (m, 2H, BBN-C*H*), 2.13 (m, 2H, N-CH$_2$CH_2), 2.72 (s, 3H, CH_3), 4.51 (s, 2H, N-CH_2), 5.09 (s, broad, 2 x 1H, B-N*H*H and B-NH*H*), 5.89 (s, broad, 1H, Zn-N*H*H), 6.09 (s, broad, 1H, Zn-NH*H*), 6.77 (s, 1H, pyrazole-C*H*), 7.46 (d, *J* = 7.7, 1H, pyridine-C*H*), 7.71 (d, *J* = 7.7, 1H, pyridine-C*H*), 8.03 (t, *J* = 7.7, 1H, pyridine-C*H*). Due to low solubility and the dynamic nature of the compound, high resolution ^{13}C NMR were challenging to obtain. The following are select resonances associated with the molecule: ^{13}C NMR (CD_2Cl_2, 25 °C) δ = 17.10, 20.79, 21.72, 24.62, 24.83, 30.46, 31.23, 33.34, 33.73, 50.69, 104.61, 119.47, 127.43, 142.74, 146.65, 159.88. Selected IR data for X = PF_6 (KBr) υ = 3301 (N-H), 3265 (N-H), 3152 (N-H), 1616, 1485, 1373, 1222, 1204, 845, 796, 558 cm^{-1}.

Transformation of [($^{n\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] to ($^{n\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) (n = 2, 3, 4) by introduction of bromide. The following is typical for all three reactions, only that with [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] is described: A 20 mL scintillation vial was charged with [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] (0.010 g, 0.015 mmol) and 1 mL DCM. While stirring, solid [Bu_4N][Br] (0.007 g, 0.022 mmol) was added. For [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] only, an immediate fine white precipitate formed (a zinc containing species resulting from demetalation). After ca. 1 min, the solution was filtered into an NMR tube and a spectrum obtained. The data revealed: for [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6], formation of two species ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) and $^{2\text{-BBN}}$NN$^{t\text{Bu}}$ (demetalated ligand) in a 66:34 ratio by ^{1}H NMR integration. For [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] and [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6], the conversion to ($^{n\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) is quantitative. If repeating the reactions involving [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] and [($^{4\text{-}}$

$^{BBN}NN^{tBu}$)ZnBr(N_2H_4)][PF_6] are repeated in THF, the following ratio of product:demetalated ligand is: **n = 2** 73:27; **n = 4** 79:21.

Reaction between ($^{butyl}NN^{tBu}$)ZnBr$_2$ and N_2H_4. A 20 mL scintillation vial was charged with ($^{butyl}NN^{tBu}$)$ZnBr_2$ (0.014 g, 0.028 mmol) and 2 mL THF. While stirring, N_2H_4 (0.159 M stock solution in THF, 0.177 mL, 0.028 mmol) resulting in the immediate precipitation of a fine white powder. After 5 min, the solution was filtered into a J-Young tube and the mixture analyzed by ^{1}H NMR spectroscopy. Authentic samples of both the starting material and free ligand, $^{butyl}NN^{tBu}$, were analyzed by ^{1}H NMR spectroscopy (THF) and the data are displayed below. Analysis of the reaction mixture revealed a ca. 1:1 ration of starting material:demetallated ligand.

Synthesis of ($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3). A 20 mL scintillation vial was charged with ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr_2$(N_2H_4) (0.214 g, 0.337 mmol) and 8 mL THF and frozen. A separate vial was charged with potassium bis(trimethylsilyl)amide (0.067 g, 0.336 mmol) and 4 mL THF and frozen. Upon thawing, the solution of $KN(SiMe_3)_2$ was added dropwise to the solution containing ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr_2$(N_2H_4) and stirred to room temperature for 15 min. The solution was filtered over Celite and dried. The resulting material was twice precipitated from THF (5 mL) with *n*-pentane (15 mL) to afford white powder (0.109 g, 0.197 mmol, 58%) assigned as ($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3). Single, X-ray quality crystals were obtained by layering a THF solution of ($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3) with hexamethyldisiloxane at room temperature. MALDI-TOF of $C_{24}H_{39}N_5Br_1B_1Zn_1$: Calc. 551.177; Found 550.842. Sample – N_2H_3: Calc. 520.147; Found 519.830. ^{1}H NMR ($CDCl_3$, 25 °C) δ = -0.11 (dd, *J* = 10.6, 13.5, 1H, B-CH*H*), 0.50 (s, 1H, N*H*), 0.66 (dt, *J* = 10.9, 13.3, 1H, B-C*H*H), 0.94 (s, 1H, *N*H), 1.50 (s, 9H, C(CH_3)$_3$), 1.57-1.70 (m, 6H, BBN-C*H*), 1.75-1.94 (m, 6H, BBN-C*H*), 2.11 (m, 1H, CH_2CH*H*CH_2), 2.40 (d, *J* = 4.6, 1H, BBN-C*H*), 2.69 (q, *J* = 13.1, 1H, CH_2C*H*HCH_2), 2.90 (s, 3H, CH_3), 3.62 (m, 1H, BBN-C*H*), 4.31 (d, *J* = 12.7, 1H, N-CH*H*), 4.50 (t, *J* = 12.7, 1H, N-C*H*H), 6.98 (s, 1H, pyrazole-C*H*), 7.45 (d, *J* = 7.7, 1H, pyridine-C*H*), 7.87 (d, *J* = 7.7, 1H, pyridine-C*H*), 8.00 (t, *J* = 7.7, 1H, pyridine-C*H*). ^{13}C NMR (THF-d_8, 25 °C) δ = 13.08 (broad, B-CH_2), 23.18 (broad, B-*C*H), 23.47 (broad, B-*C*H), 23.74, 23.91, 25.92, 26.59, 29.44 (C(*C*H_3)$_3$), 31.49, 31.85, 32.52 (*C*(CH_3)$_3$), 33.61, 34.16, 55.09 (N-*C*H_2), 103.01 (pyrazole-*C*H), 118.64 (pyridine-*C*H), 125.94 (pyridine-*C*H), 141.51 (pyridine-*C*H), 146.72, 147.66, 158.52, 159.64. ^{11}B NMR (THF-d_8, 25 °C) δ = -5.56. Selected IR data (ATR, neat) υ = 3325 (N-H), 3301 (N-H), 3261 (N-H), 3217 (N-H), 3141 (N-H), 3075, 1611, 1577, 1481, 1371, 1242, 1201, 797 cm^{-1}. **Alternate synthesis from [($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_4)][OTf].** A 20 mL scintillation vial was charged with [($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_4)][OTf] (0.020 g, 0.029 mmol) and 2 mL THF and frozen. A separate vial was charged with $KN(SiMe_3)_2$ (0.006 g, 0.029 mmol) and 1 mL THF and frozen. Upon thawing, the solution of $KN(SiMe_3)_2$ was added to the vial of [($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_4)][OTf] and stirred for 15 min. The solution was filtered over Celite and dried. Analysis of ^{1}H NMR (THF) revealed the desired product, ($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3), and demetallated ligand, ($^{3\text{-}BBN}NN^{tBu}$), to be present in approx. 1:1 ratio. Therefore, for bulk preparation of ($^{3\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3), the method from ($^{3\text{-}BBN}NN^{tBu}$)$ZnBr_2$(N_2H_4) was employed.

Attempted Synthesis of ($^{2\text{-}BBN}NN^{tBu}$)ZnBr(N_2H_3). A 20 mL scintillation vial was charged with ($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2$ (0.056 g, 0.095 mmol) and 4 mL THF. While stirring, hydrazine (0.159 M solution in THF, 0.598 mL, 0.095 mmol) was added to generate ($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2$(N_2H_4) in situ. After stirring for 2 min, the solution was frozen. A separate vial was charged with $KN(SiMe_3)_2$ (0.019 g, 0.095 mmol) and 2 mL THF and frozen. Upon thawing, the solution containing $KN(SiMe_3)_2$ was added to the zinc containing solution. After stirring for 15 min, the solution was filtered over Celite and dried. Analysis by ^{1}H NMR (THF) revealed only resonances consistent with demetallated ligand, ($^{2\text{-}BBN}NN^{tBu}$). There was no evidence of formation of the desired product.

Attempted Synthesis of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3). Two separate routes were attempted to form this compound. Neither route enabled isolation of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3). **Route 1: one-pot method**. A 20 mL scintillation vial was charged with ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2 (0.176 g, 0.285 mmol) and 6 mL THF. While stirring, N_2H_4 (0.159 M stock solution in THF, 0.285 mmol) was added and the mixture stirred for 5 min then frozen. A separate vial was charged with K(SiMe_3)$_2$ (0.056 g, 0.281 mmol) and 2 mL THF and frozen. Upon thawing, the solution containing K(SiMe_3)$_2$ was added dropwise to the solution containing Zn. The mixture was stirred for 20 min, filtered, and dried. The solid was washed with 10 mL *n*-pentane. The material was investigated by ^{1}H NMR (THF-d_8 and C_6D_6, separately) and revealed multiple species. Sample spectra are included below. Notably, attempts to redissolve the dried material in THF after filtration resulted in insoluble materials suggesting that the material was continually degrading. Because of this, recrystallization attempts did not improve purity. **Route 2: deprotonation of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4).** A 20 mL scintillation vial was charged with ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4) (0.158 g, 0.244 mmol) and 10 mL THF and frozen. A separate vial was charged with K(SiMe_3)$_2$ (0.048 g, 0.241 mmol) and 2 mL THF and frozen. Upon thawing, the solution containing K(SiMe_3)$_2$ was added to the vial containing Zn. The mixture was stirred 20 min, filtered, and dried. The material was investigated by ^{1}H NMR spectroscopy (THF) and revealed multiple species. A representative spectrum is included below. The same issues with redissolution described above occurred with material from this reaction.

Protonation of ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3) to regenerate [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]. A 20 mL scintillation vial was charged with ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3) (0.016 g, 0.029 mmol) and 0.8 mL THF-d_8. While stirring, diphenylammonium triflate (0.0092 g, 0.029 mmol) was added and stirred 15 min. The solution was transferred to a ^{1}H NMR tube and a spectrum recorded. The data revealed clean conversion to [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] and the production of diphenylamine. The crude spectrum is included below.

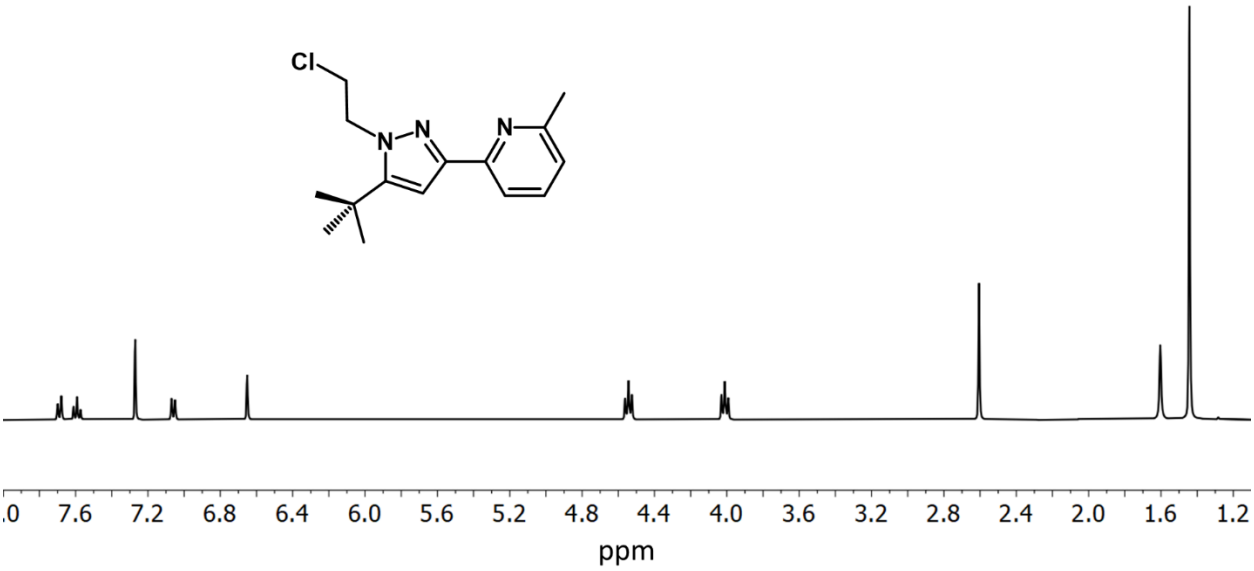


Figure S1 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 2-(5-(*tert*-butyl)-1-(2-chloroethyl)-1*H*-pyrazol-3-yl)-6-methylpyridine ($^{chloroethyl}NN^{tBu}$).

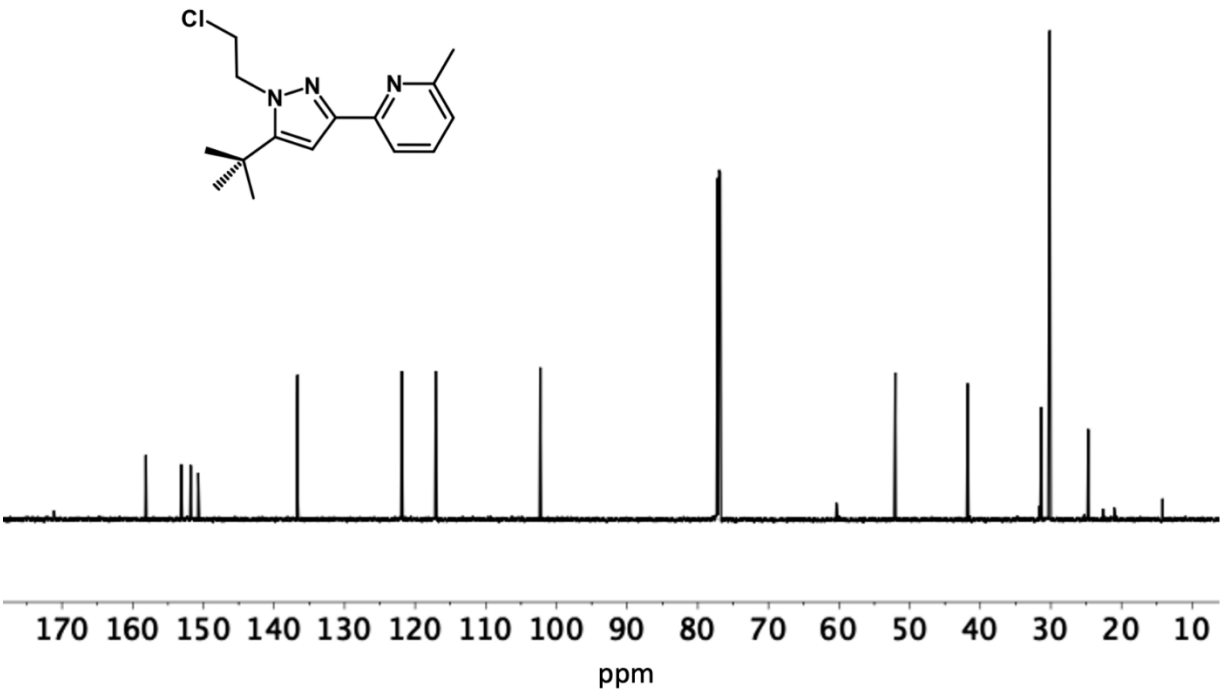


Figure S2 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 2-(5-(*tert*-butyl)-1-(2-chloroethyl)-1*H*-pyrazol-3-yl)-6-methylpyridine.

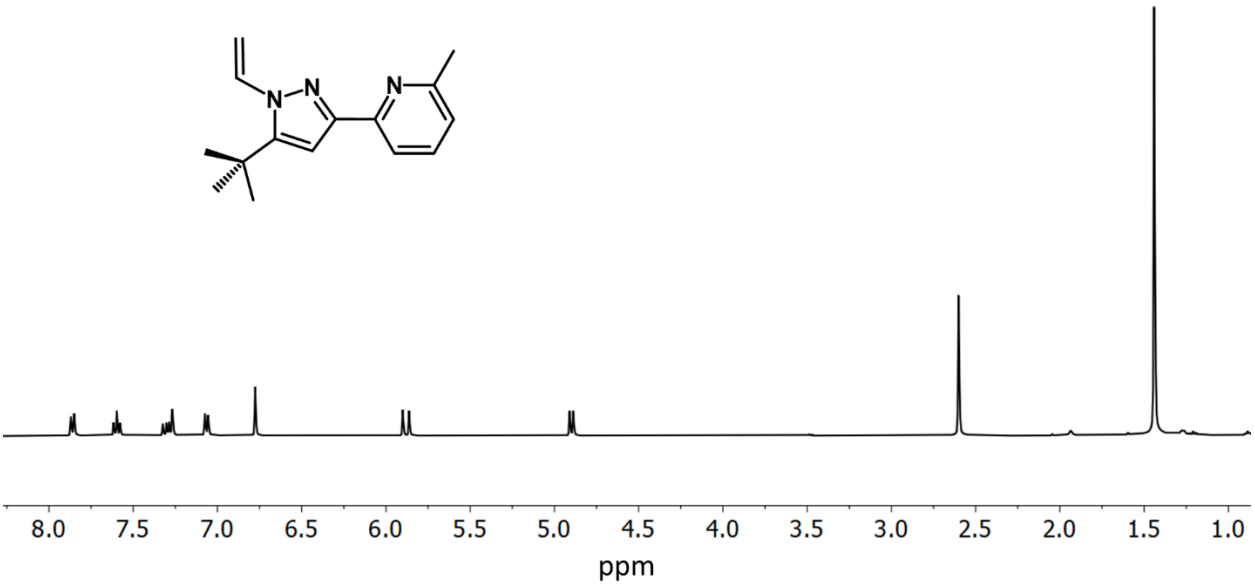


Figure S3 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 2-(5-(*tert*-butyl)-1-vinyl-1*H*-pyrazol-3-yl)-6-methylpyridine ($^{vinyl}NN^{tBu}$).

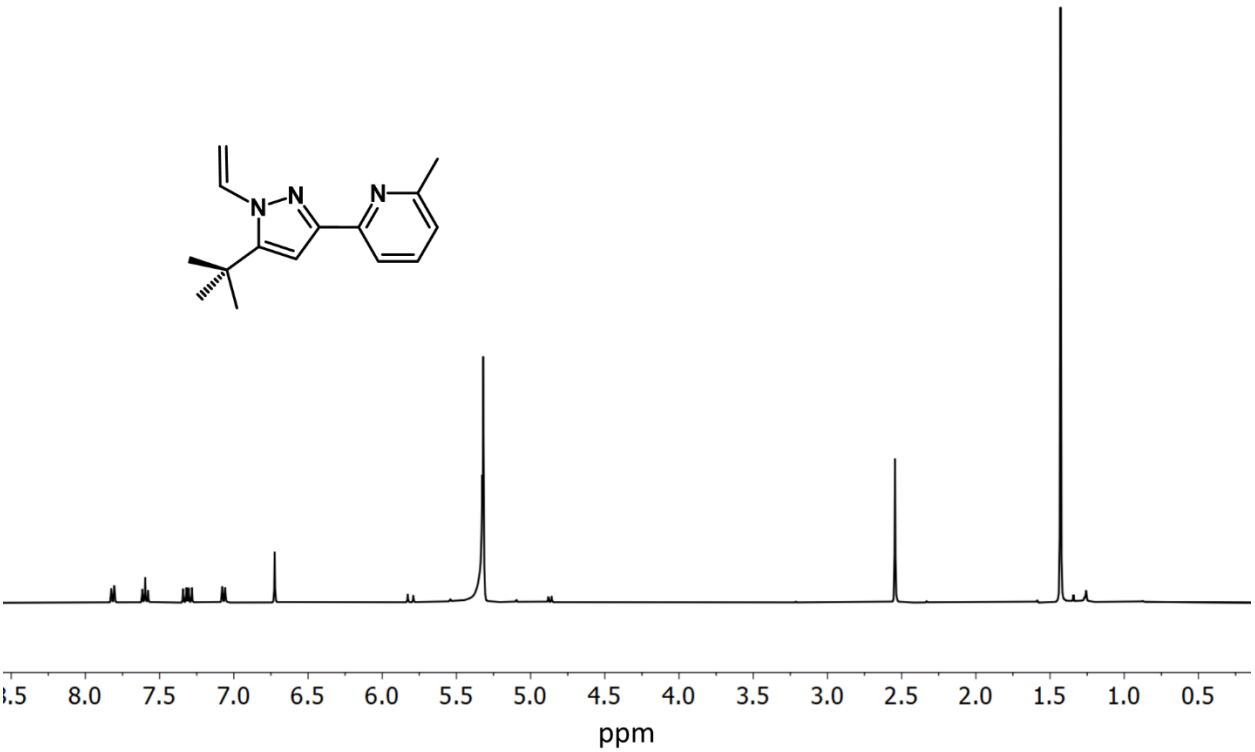


Figure S4 ^{1}H NMR spectrum (CH_2Cl_2, 25 °C) of 2-(5-(*tert*-butyl)-1-vinyl-1*H*-pyrazol-3-yl)-6-methylpyridine ($^{vinyl}NN^{tBu}$).

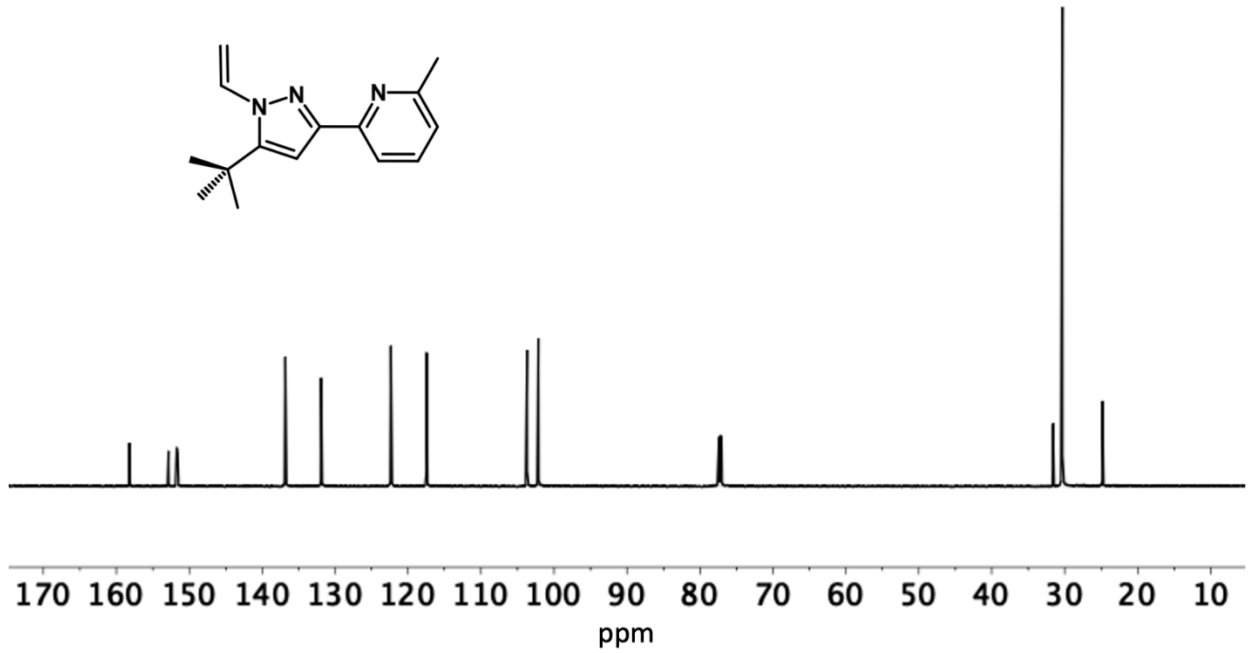


Figure S5 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 2-(5-(*tert*-butyl)-1-vinyl-1*H*-pyrazol-3-yl)-6-methylpyridine.

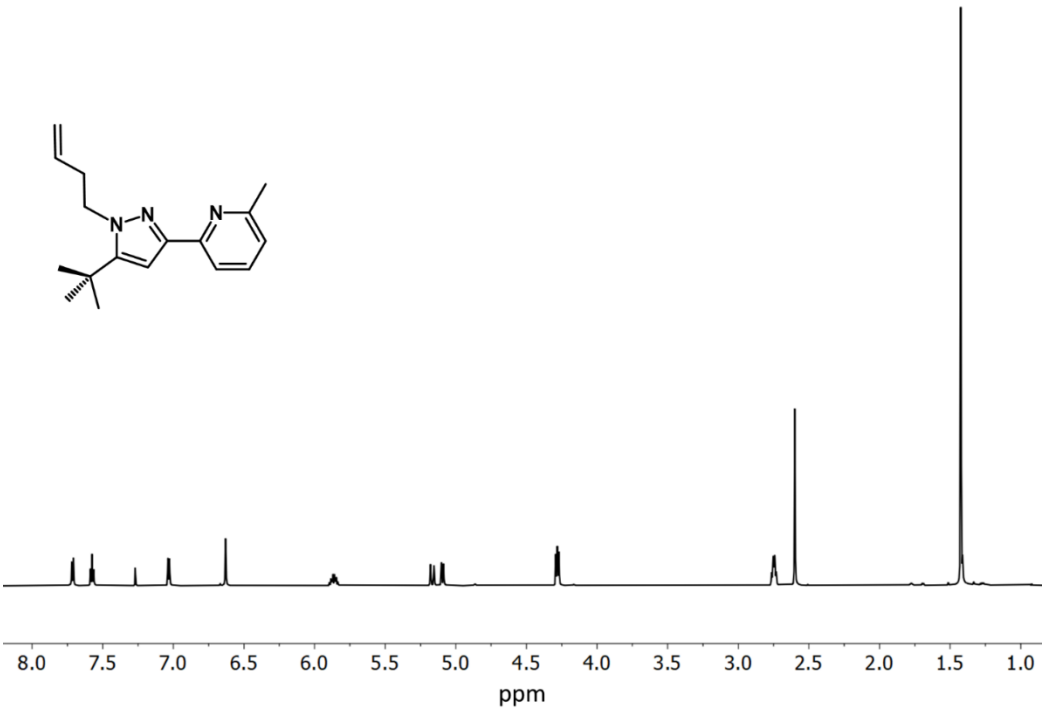


Figure S6 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of 2-(1-(but-3-en-1-yl)-5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-6-methylpyridine ($^{butenyl}NN^{tBu}$).

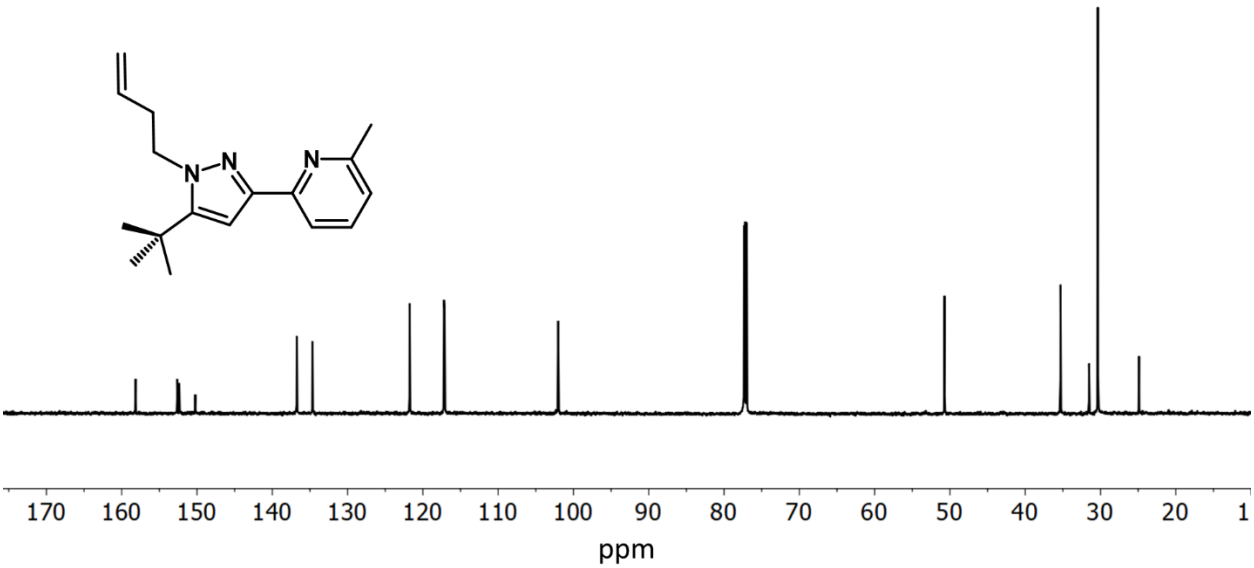


Figure S7 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of 2-(1-(but-3-en-1-yl)-5-(*tert*-butyl)-1*H*-pyrazol-3-yl)-6-methylpyridine ($^{butenyl}NN^{tBu}$).

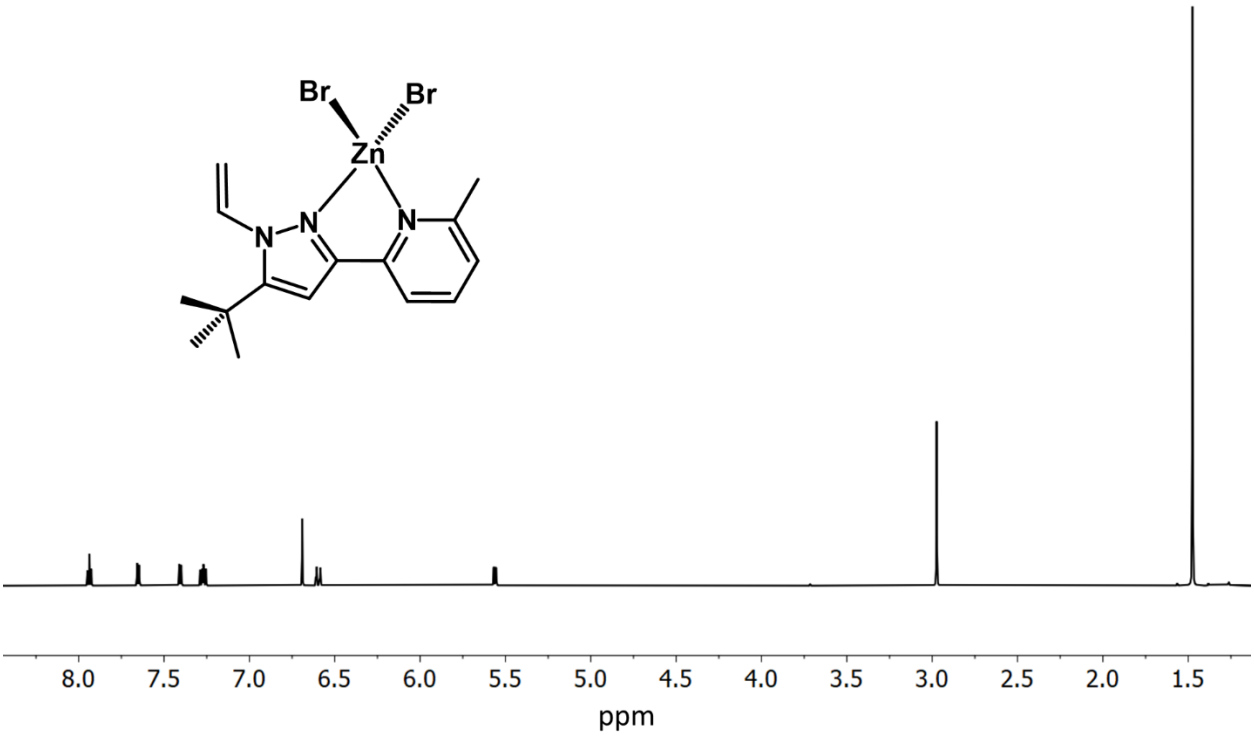


Figure S8 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{vinyl}NN^{tBu}$)$ZnBr_2$.

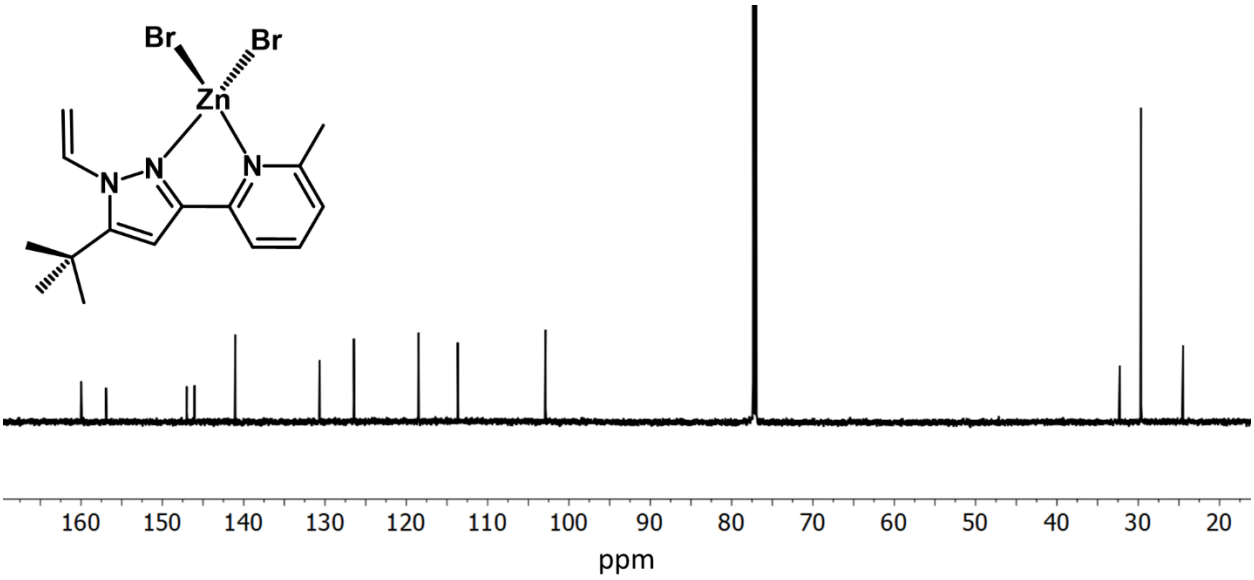


Figure S9 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{vinyl}NN^{tBu}$)$ZnBr_2$.

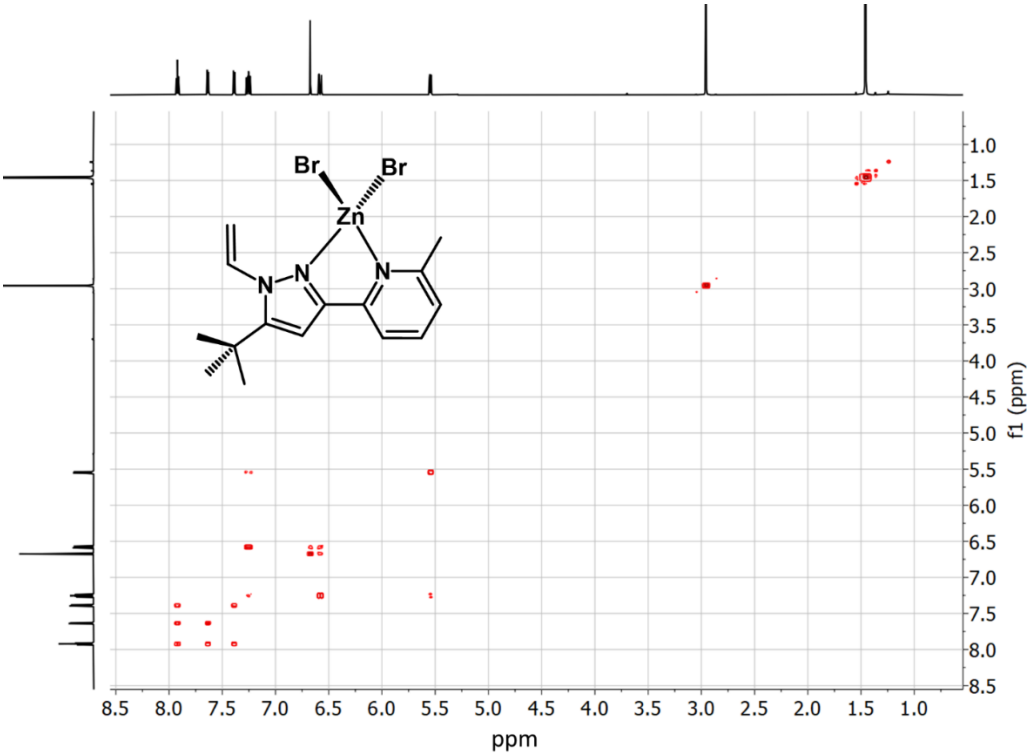


Figure S10 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C) of ($^{vinyl}NN^{tBu}$)$ZnBr_2$.

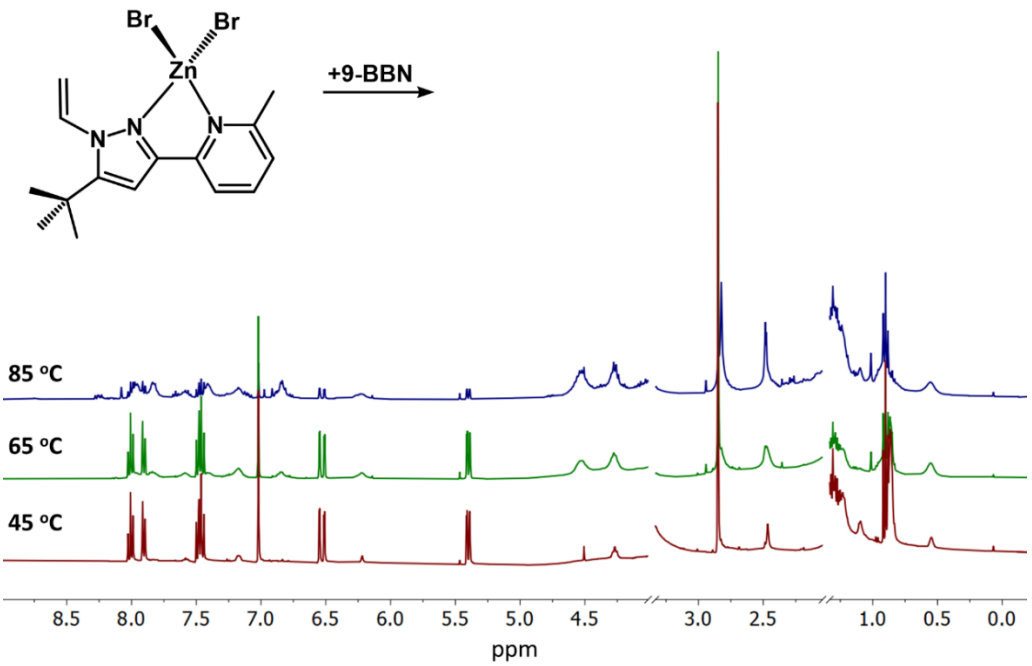


Figure S11 ^{1}H NMR spectra (THF) recorded at 25 °C of attempted hydroboration of (^{vinyl}NN^{tBu})ZnBr$_2$. These were three separate sample tubes analyzed at the illustrated temperatures. For more information, see text above.

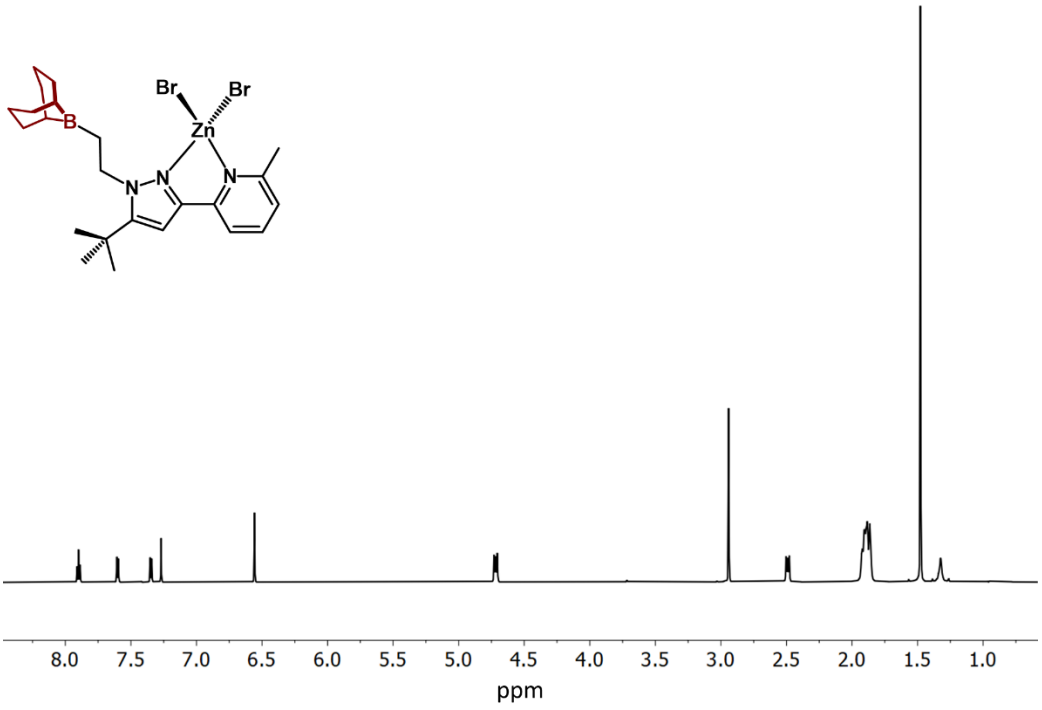


Figure S12 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$.

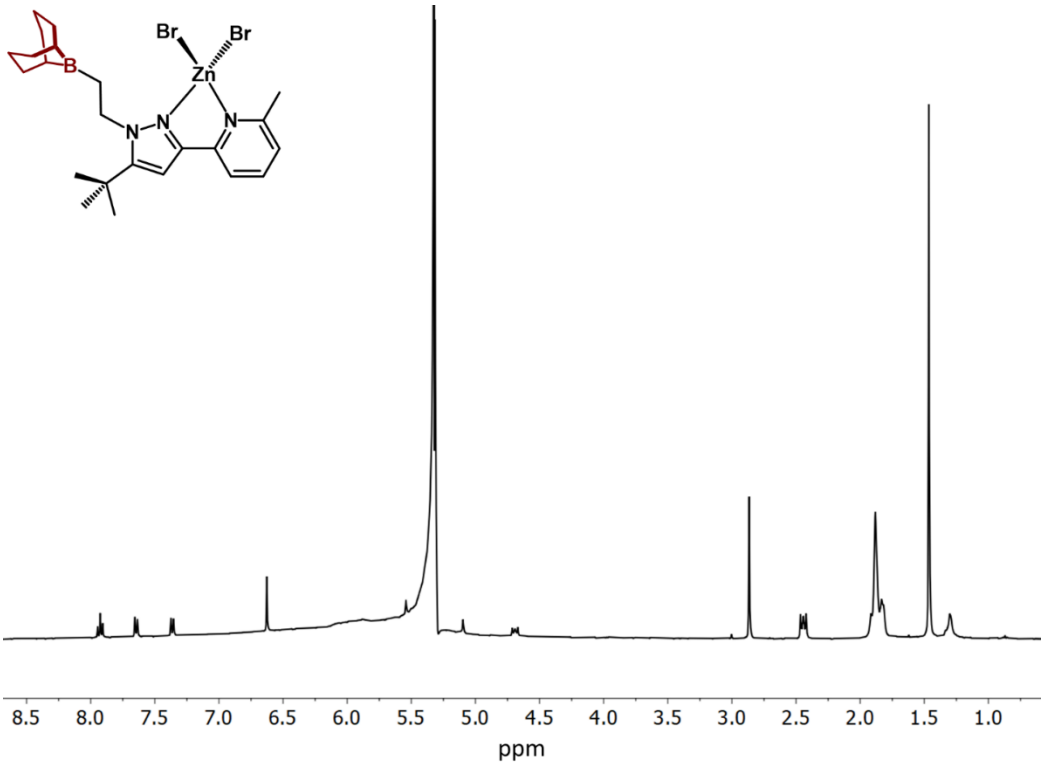


Figure S13 ^{1}H NMR spectrum (CH_2Cl_2, 25 °C) of ($^{2\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

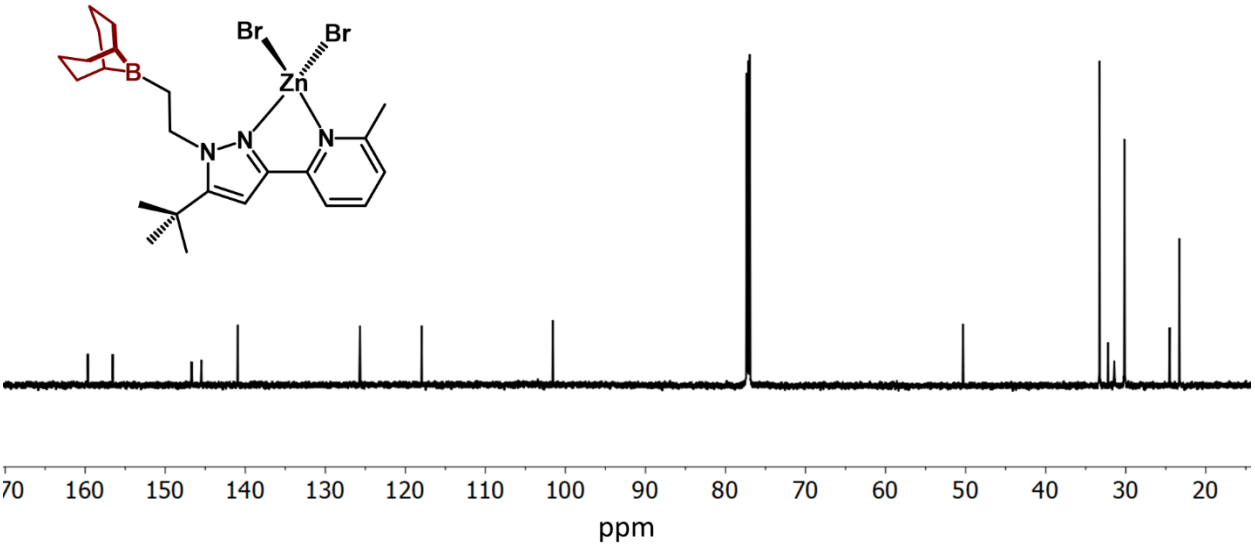


Figure S14 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{2\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

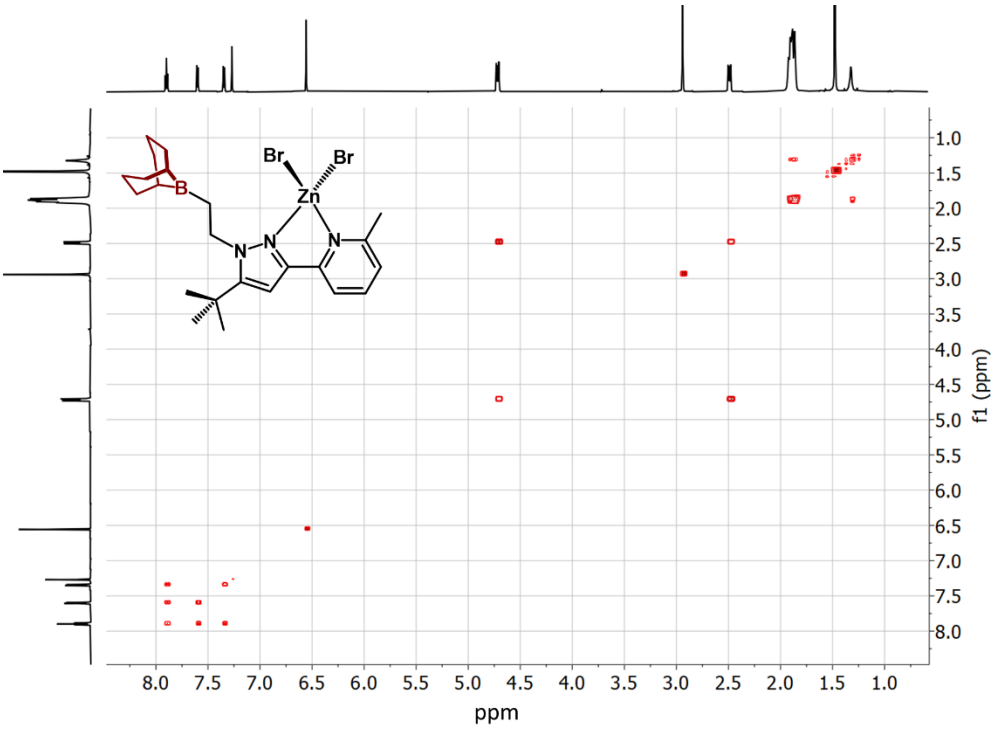


Figure S15 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C) of ($^{2\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

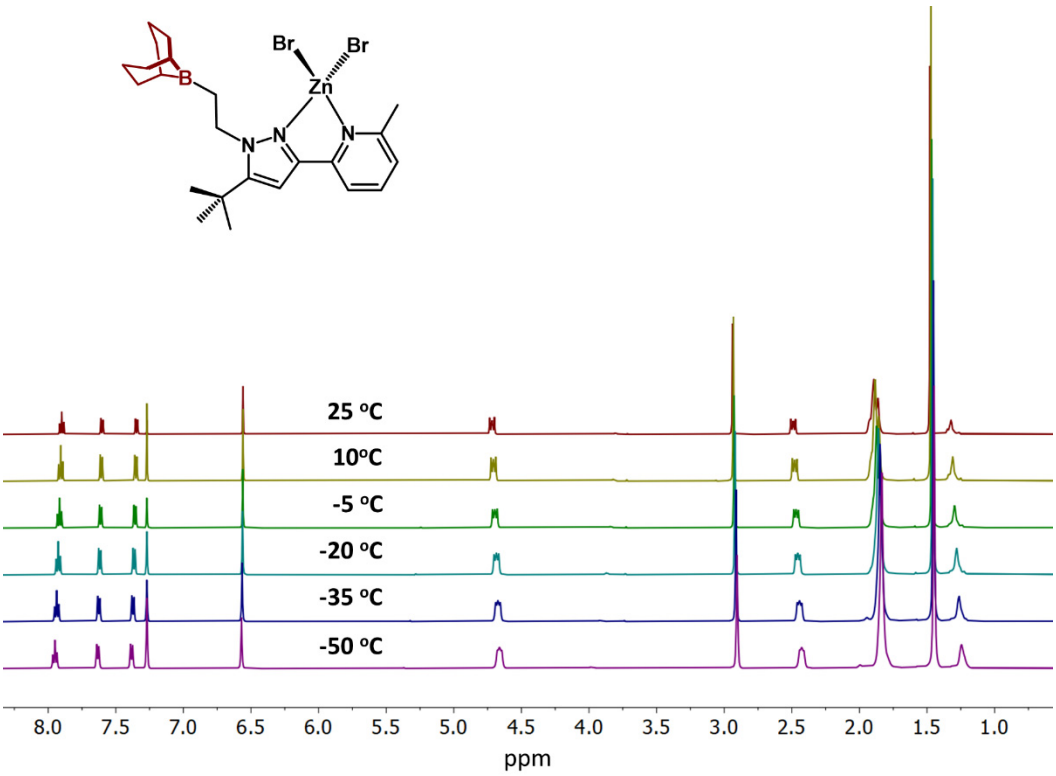


Figure S16 Variable temperature ^{1}H NMR spectra ($CDCl_3$) of ($^{2\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

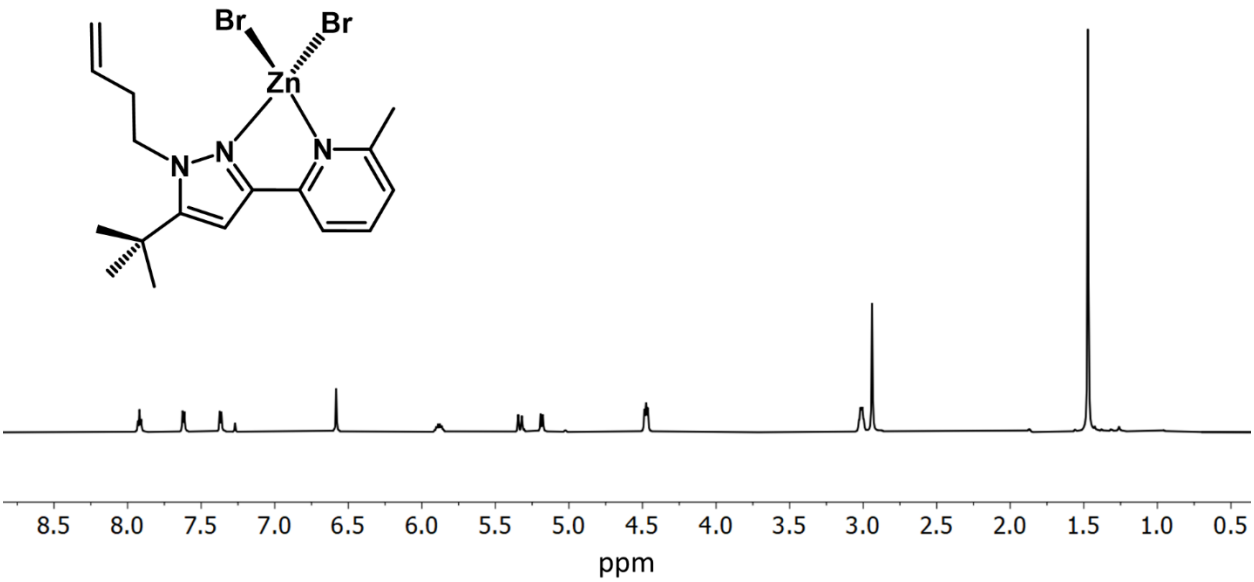


Figure S17 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{butenyl}NN^{tBu}$)$ZnBr_2$.

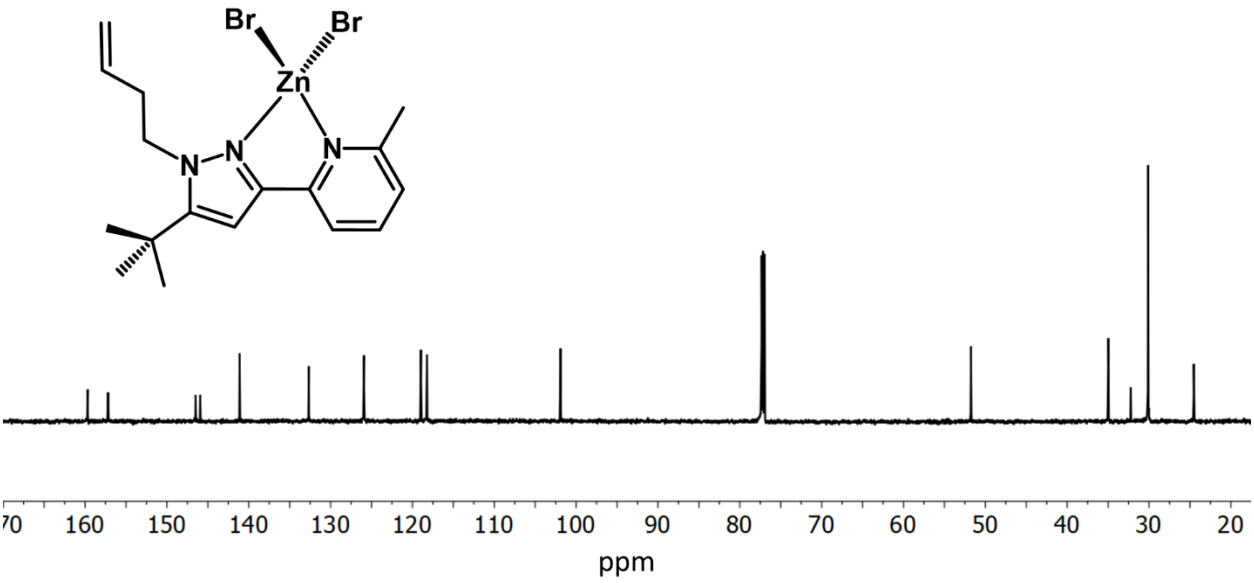


Figure S18 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{butenyl}NN^{tBu}$)$ZnBr_2$.

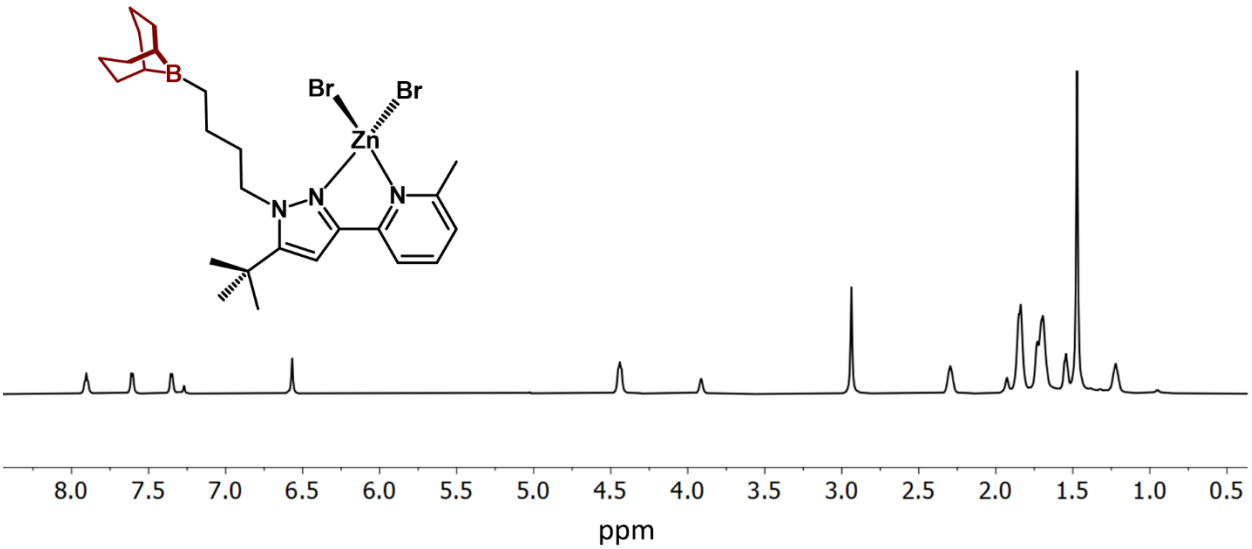


Figure S19 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

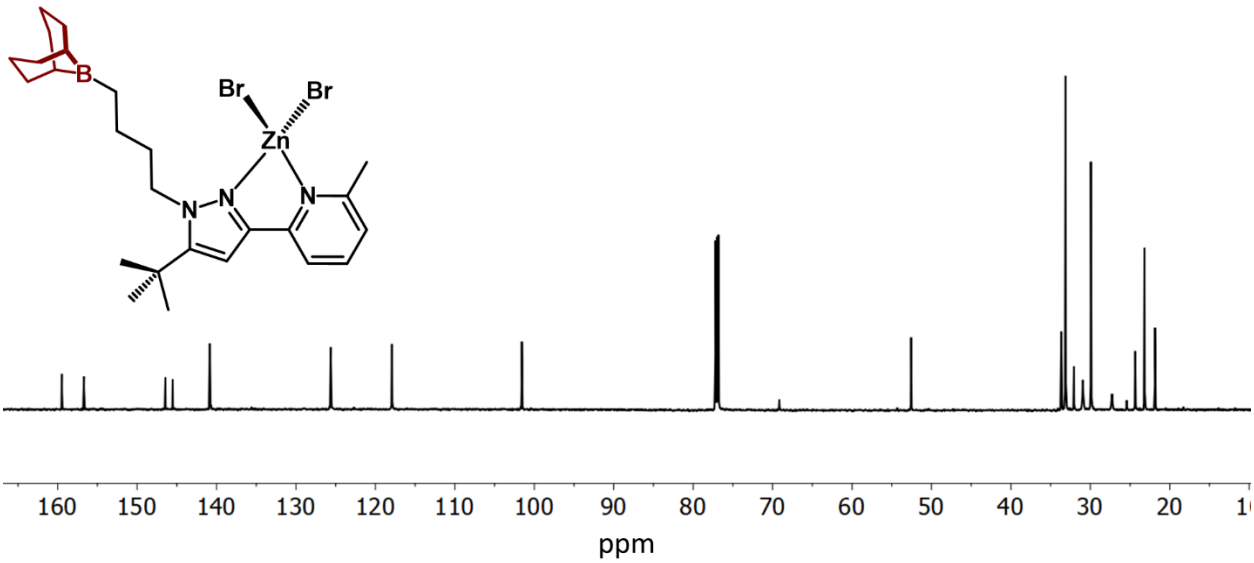


Figure S20 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

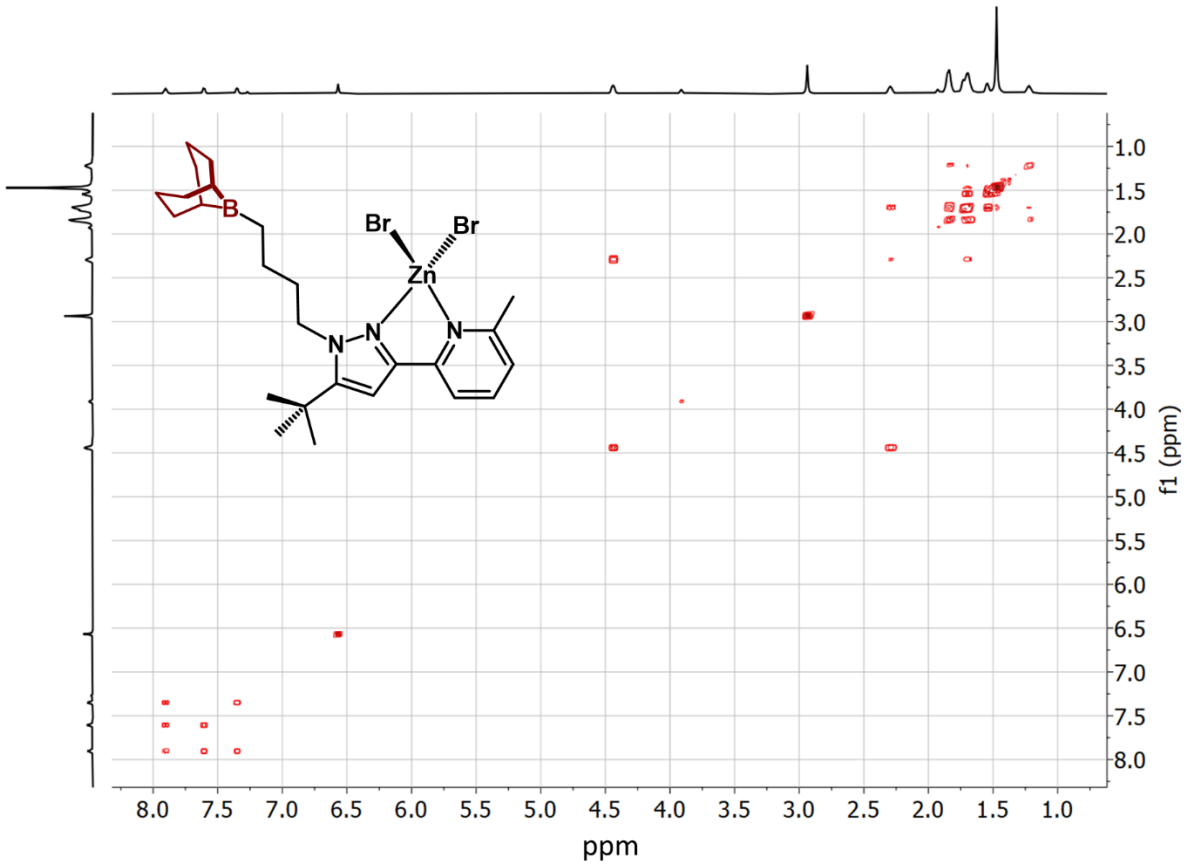


Figure S21 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2$.

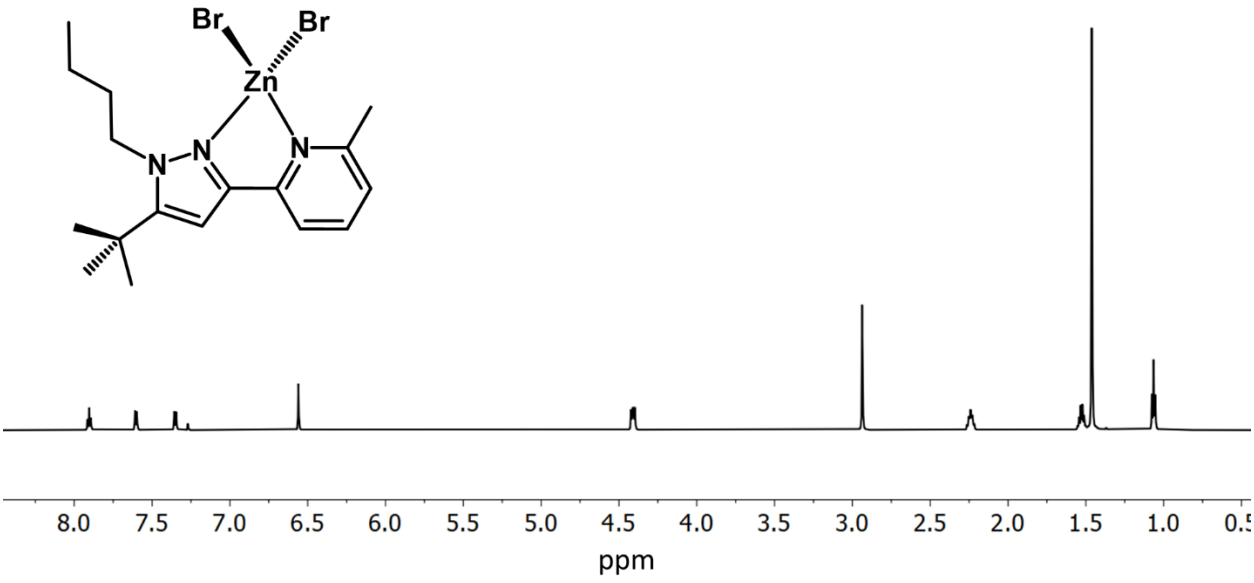


Figure S22 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{\text{butyl}}NN^{t\text{Bu}}$)$ZnBr_2$.

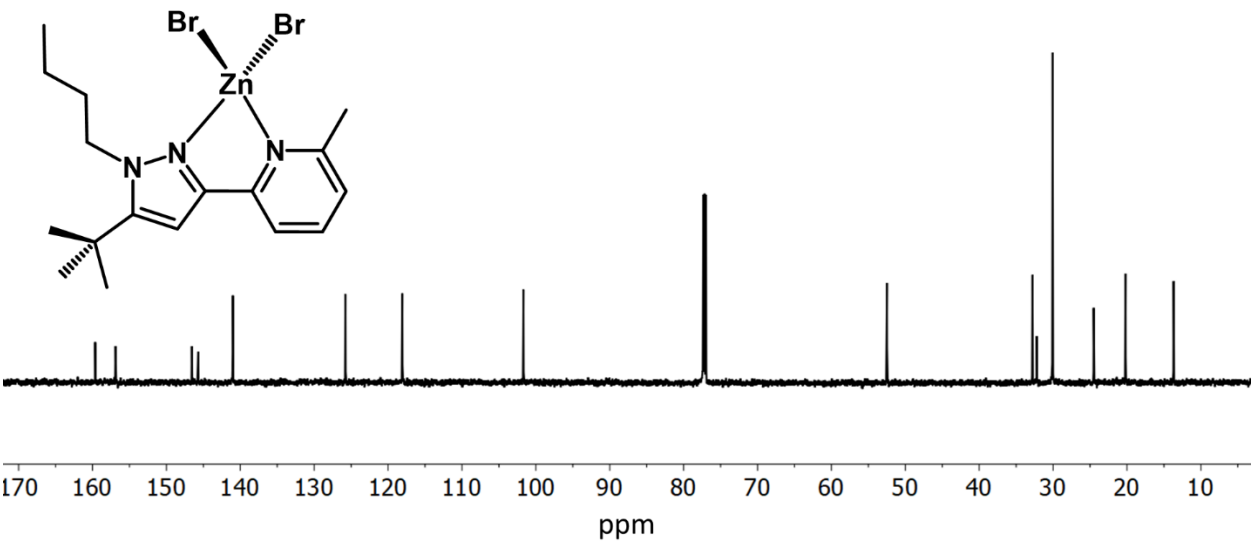


Figure S23 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{butyl}NN^{tBu}$)$ZnBr_2$.

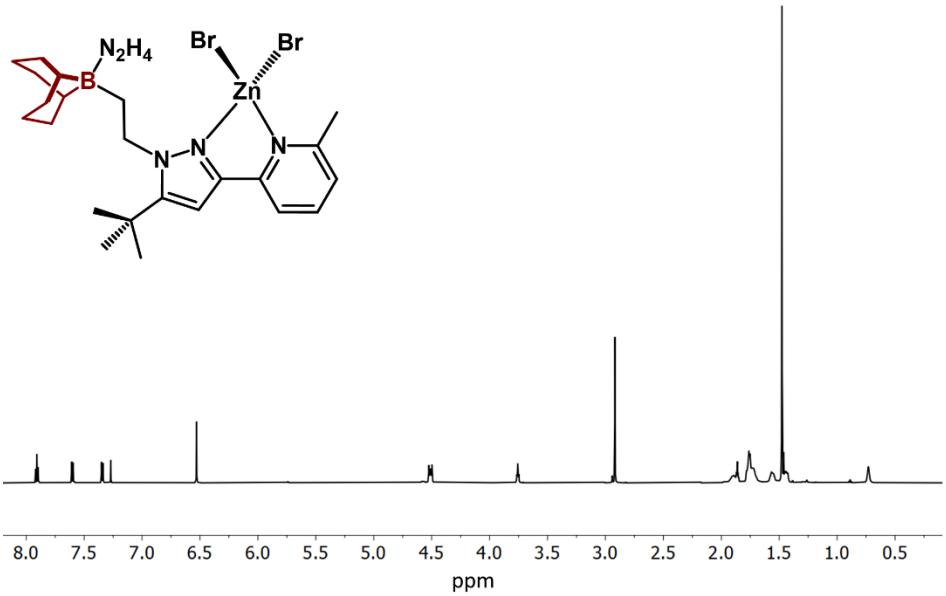


Figure S24 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{2\text{-}BBN}NN^{tBu}$)$ZnBr_2(N_2H_4)$.

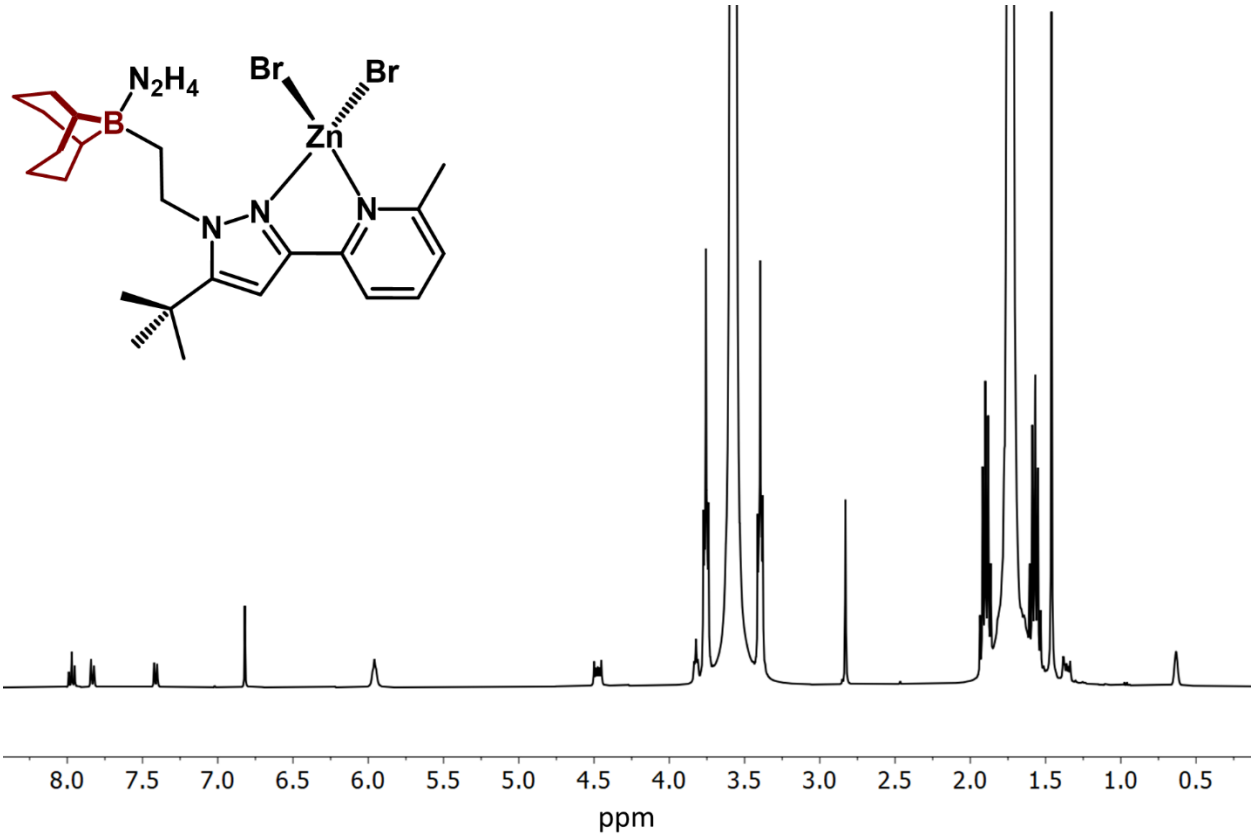


Figure S25 ^{1}H NMR spectrum (THF, 25 °C) of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$).

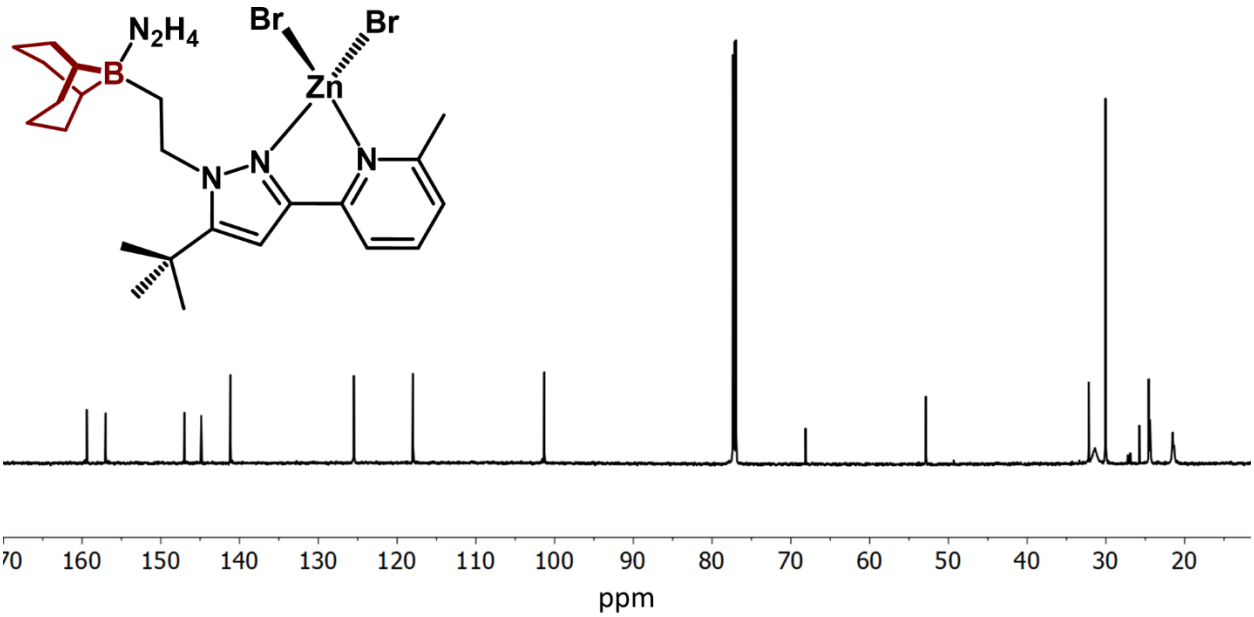


Figure S26 ^{13}C NMR spectrum (CDCl$_3$, 25 °C) of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$).

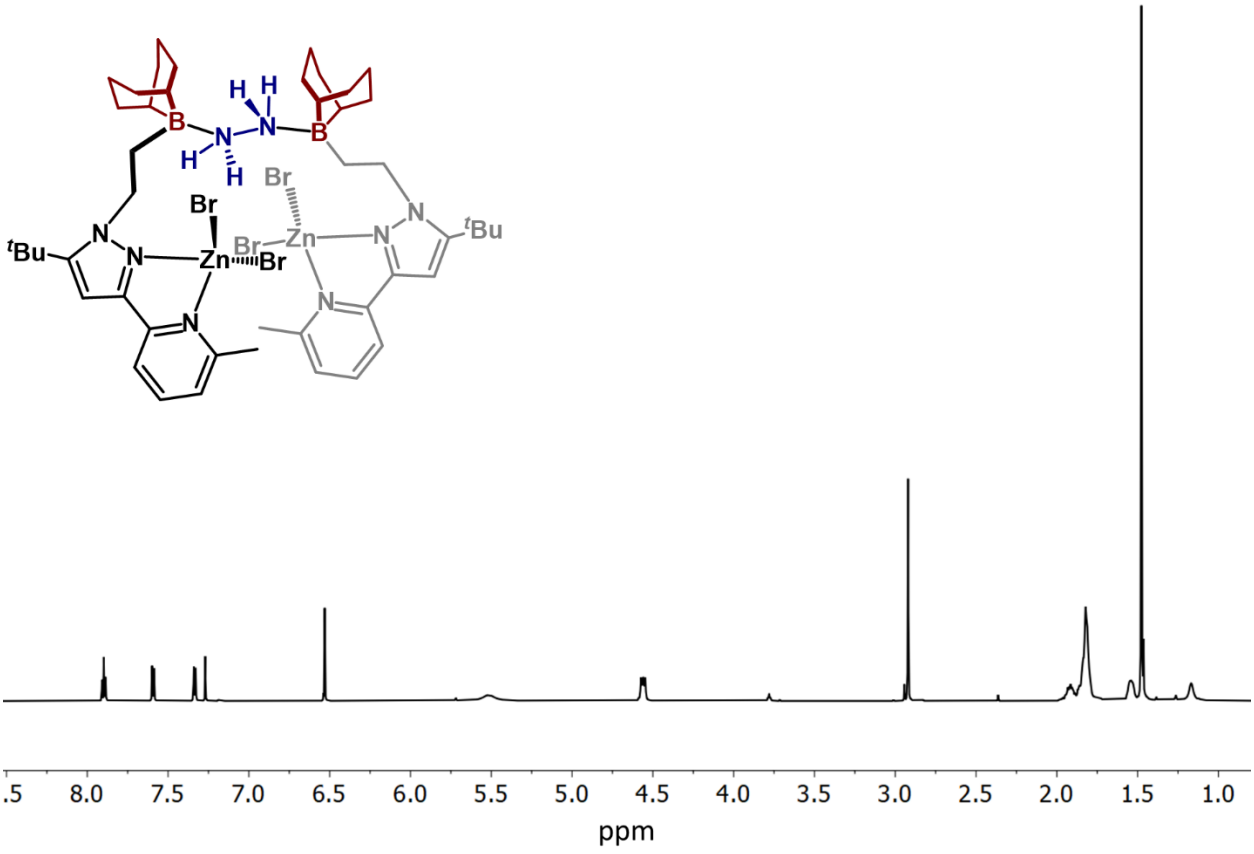


Figure S27 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of $[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr_2]_2(N_2H_4)$.

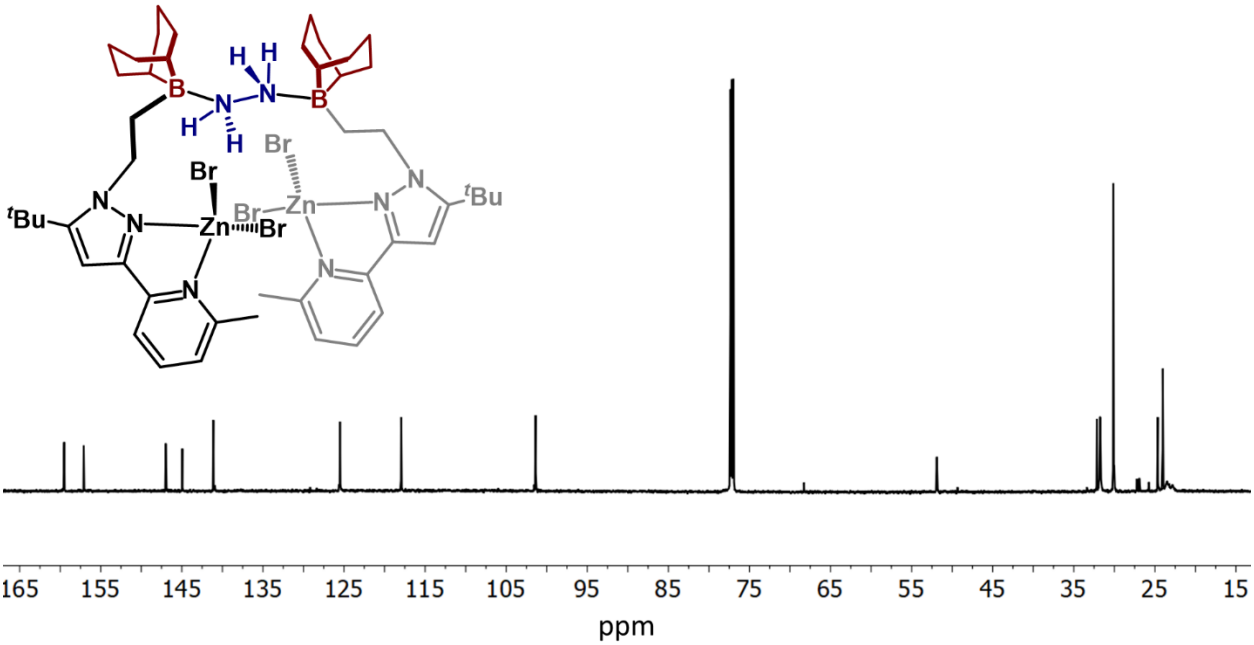


Figure S28 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of $[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr_2]_2(N_2H_4)$.

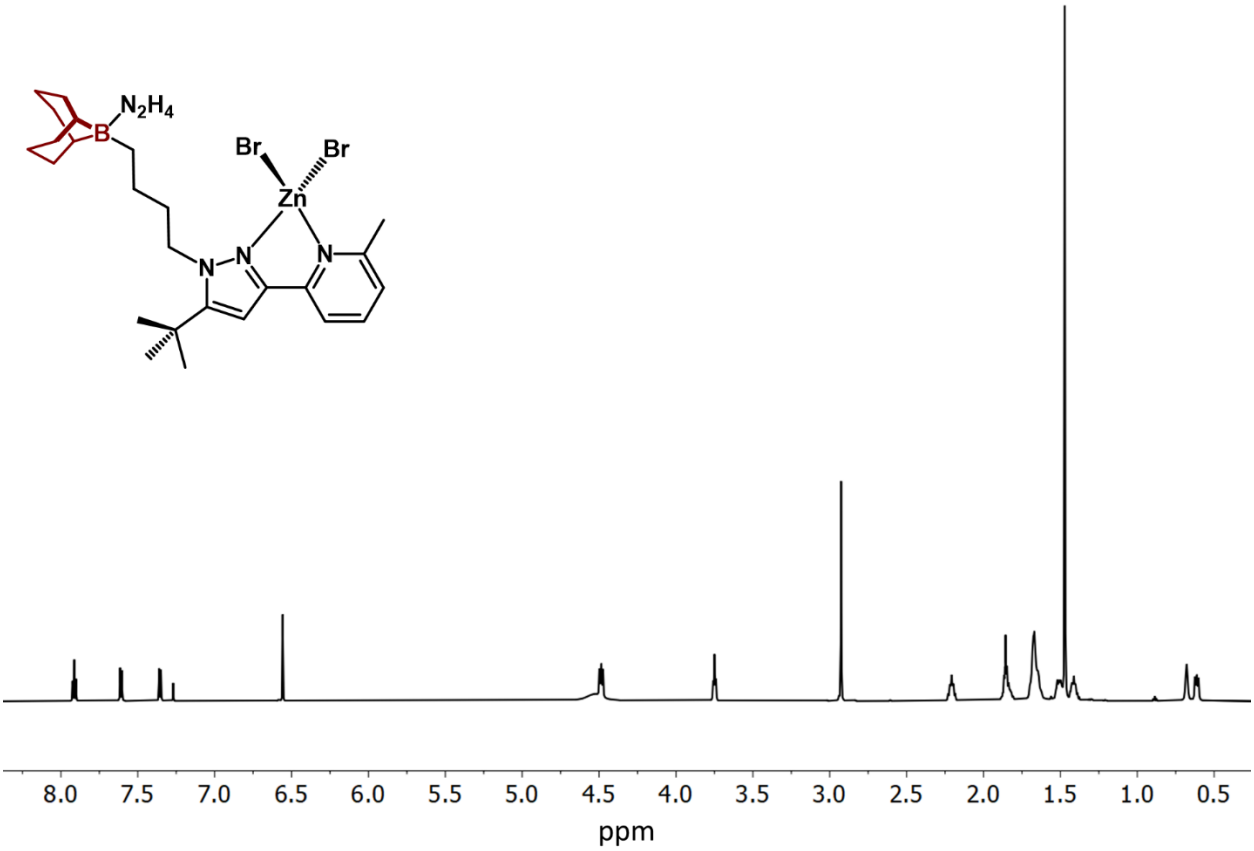


Figure S29 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$.

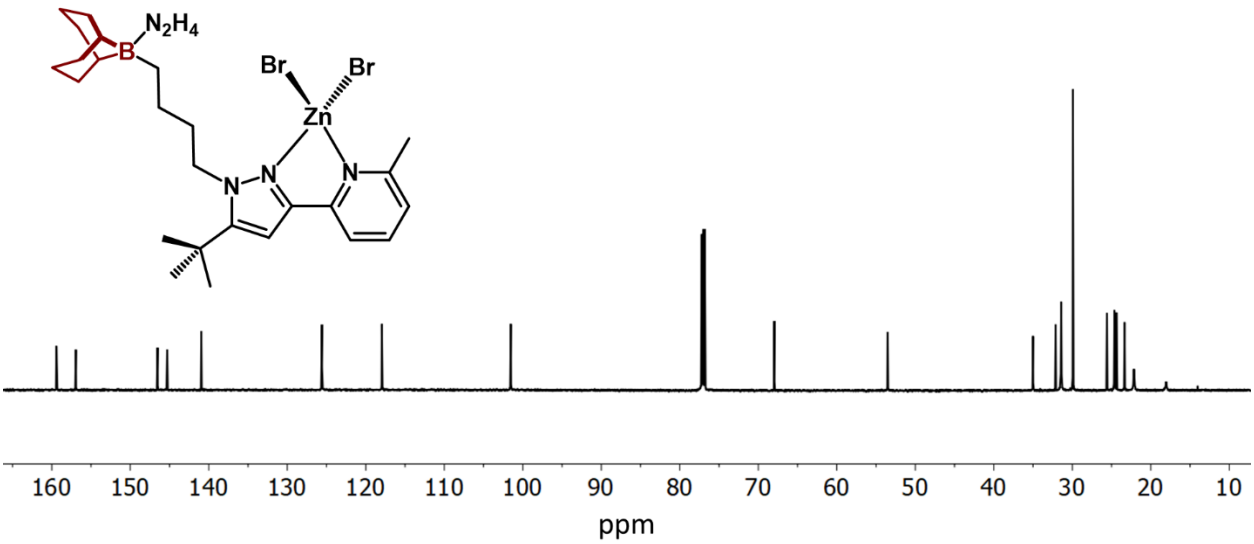


Figure S30 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$.

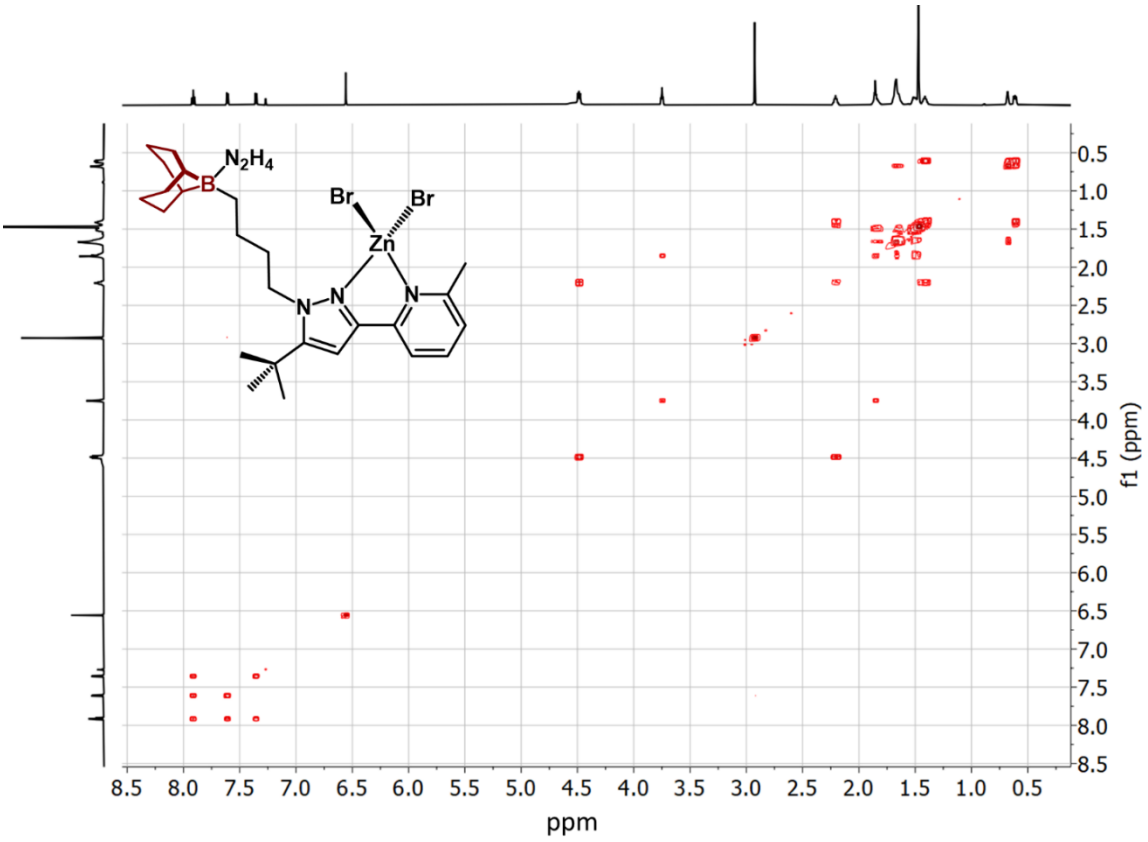


Figure S31 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, 25 °C) of ($^{4\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$.

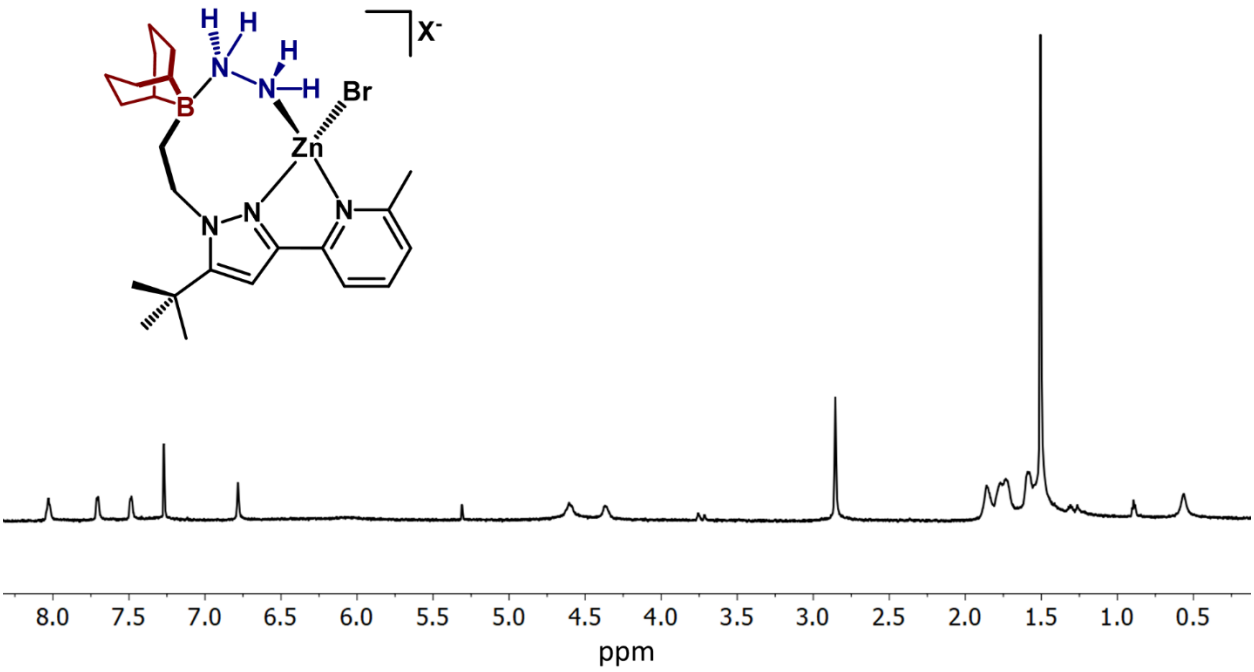


Figure S32 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of [($^{2\text{-BBN}}NN^{t\text{Bu}}$)$ZnBr(N_2H_4)$][$PF_6$].

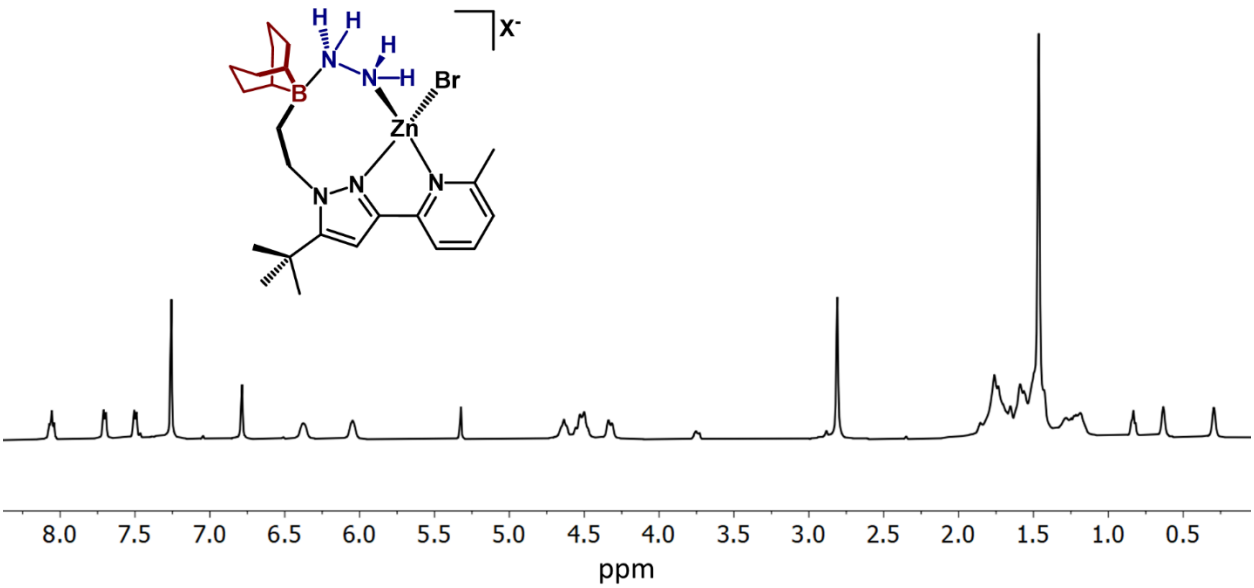


Figure S33 ^{1}H NMR spectrum ($CDCl_3$, -50 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

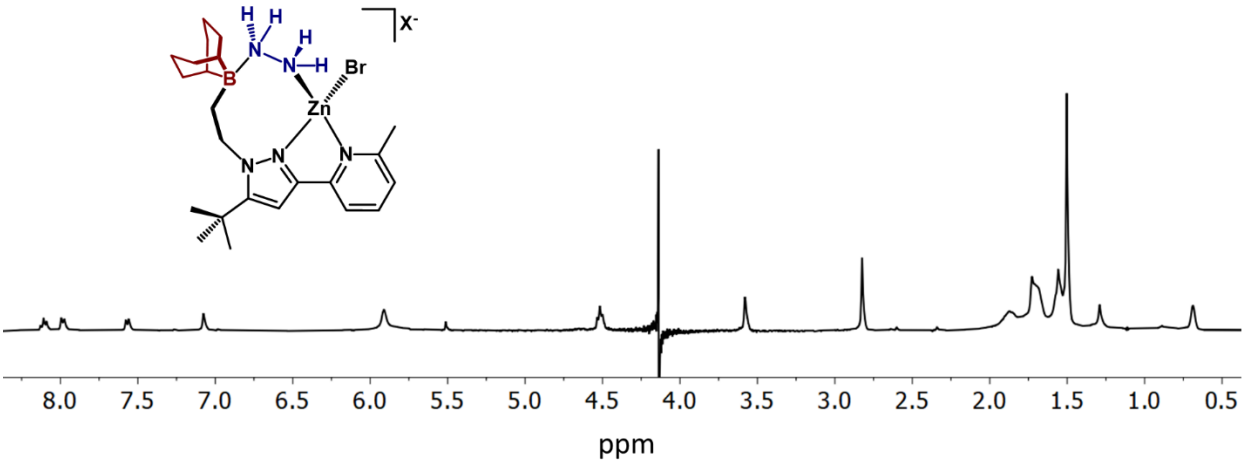


Figure S34 ^{1}H NMR spectrum (THF-d_8, 25 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]. The feature near 4.1 ppm is an artifact of the instrument.

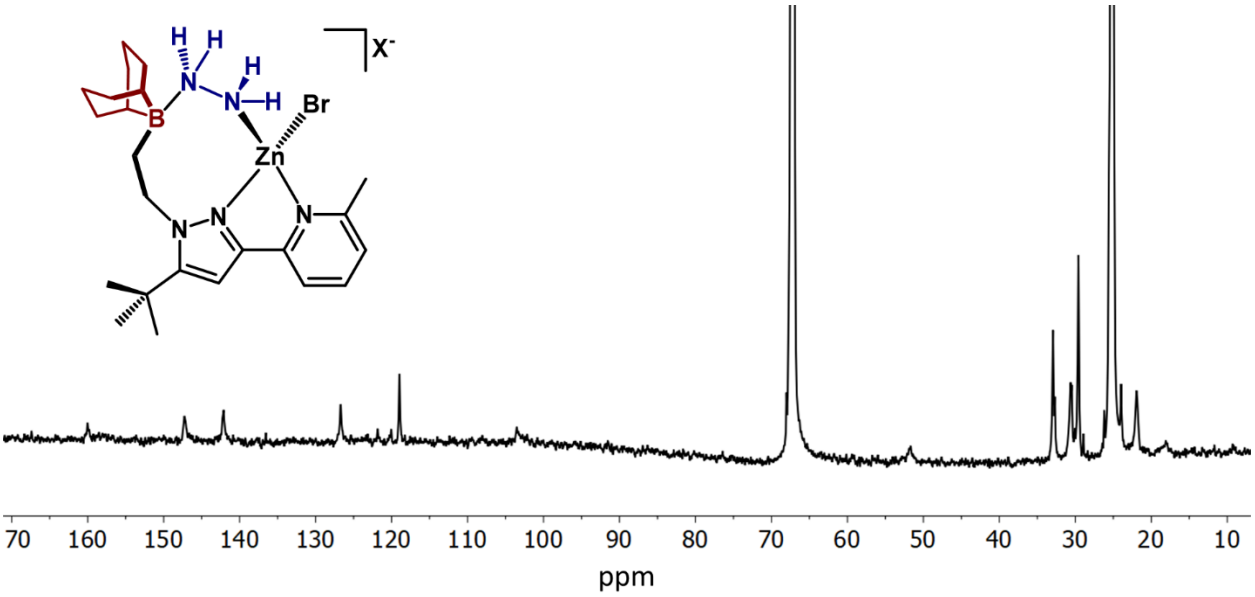


Figure S35 ^{13}C NMR spectrum (THF-d_8, 25 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf].

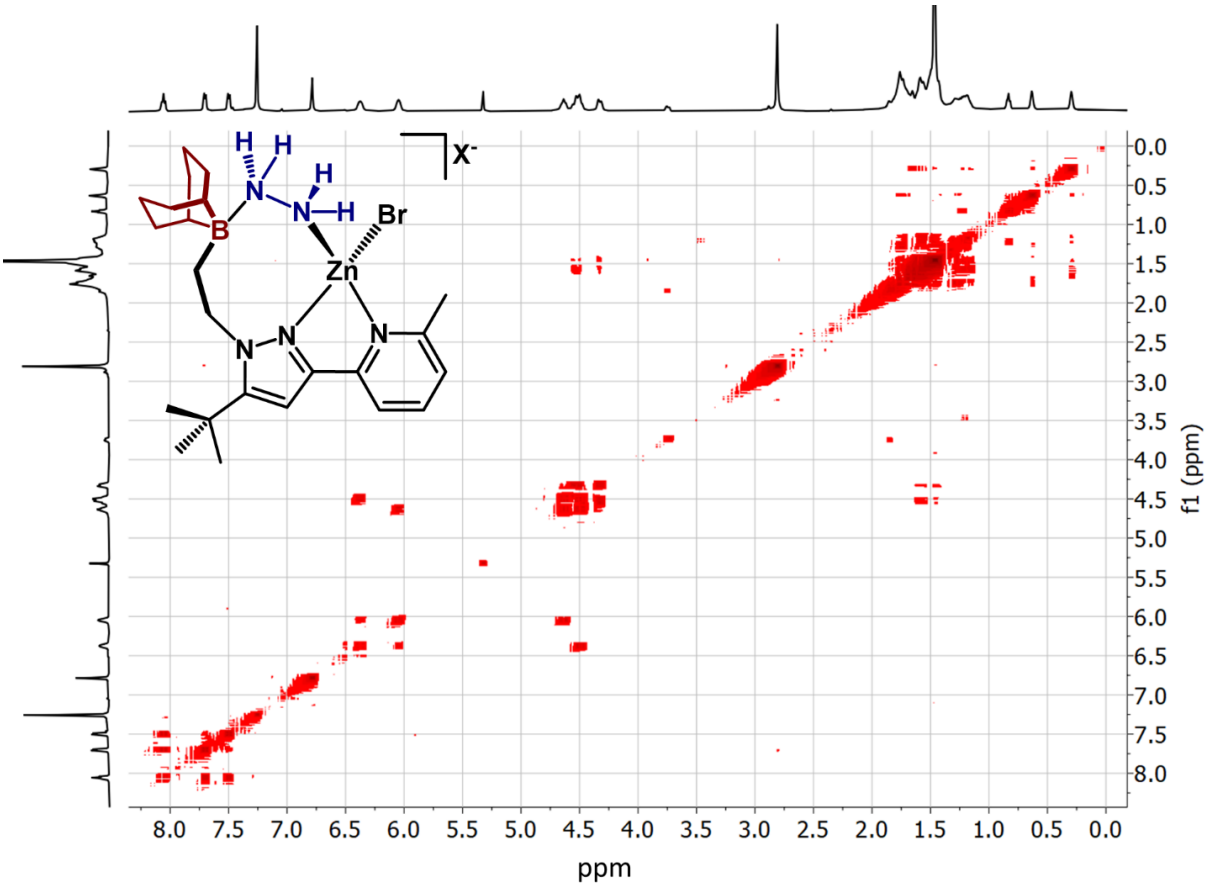


Figure S36 ^{1}H-^{1}H COSY spectrum ($CDCl_3$, -50 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

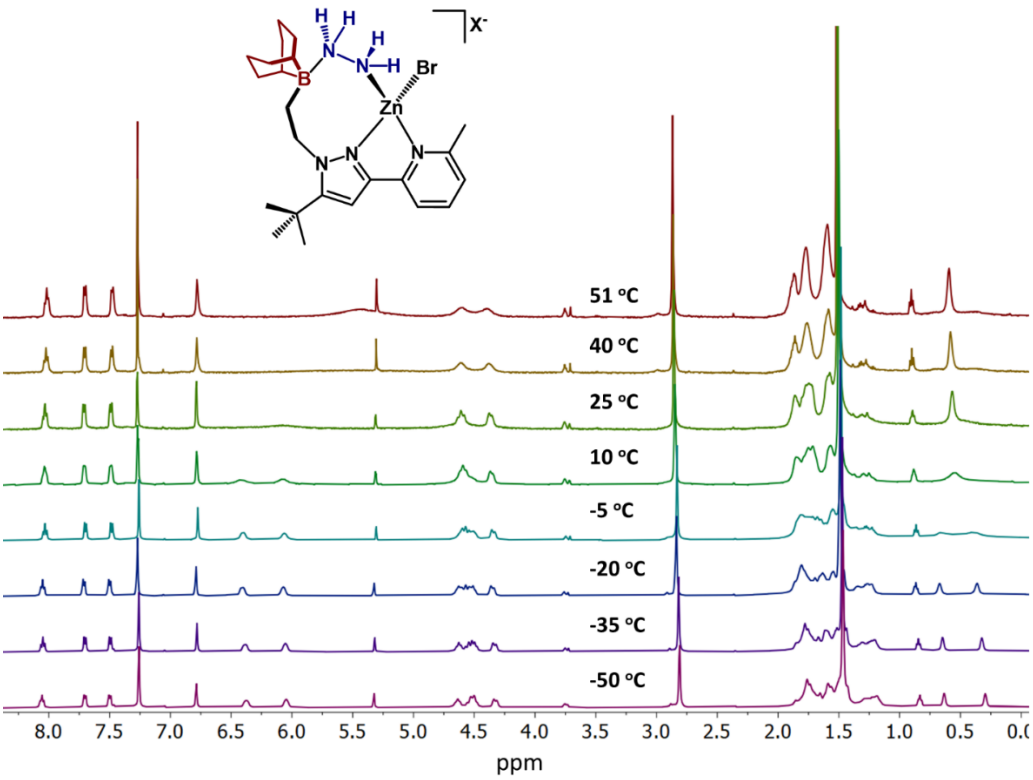


Figure S37 Variable temperature ^{1}H NMR spectra ($CDCl_3$) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

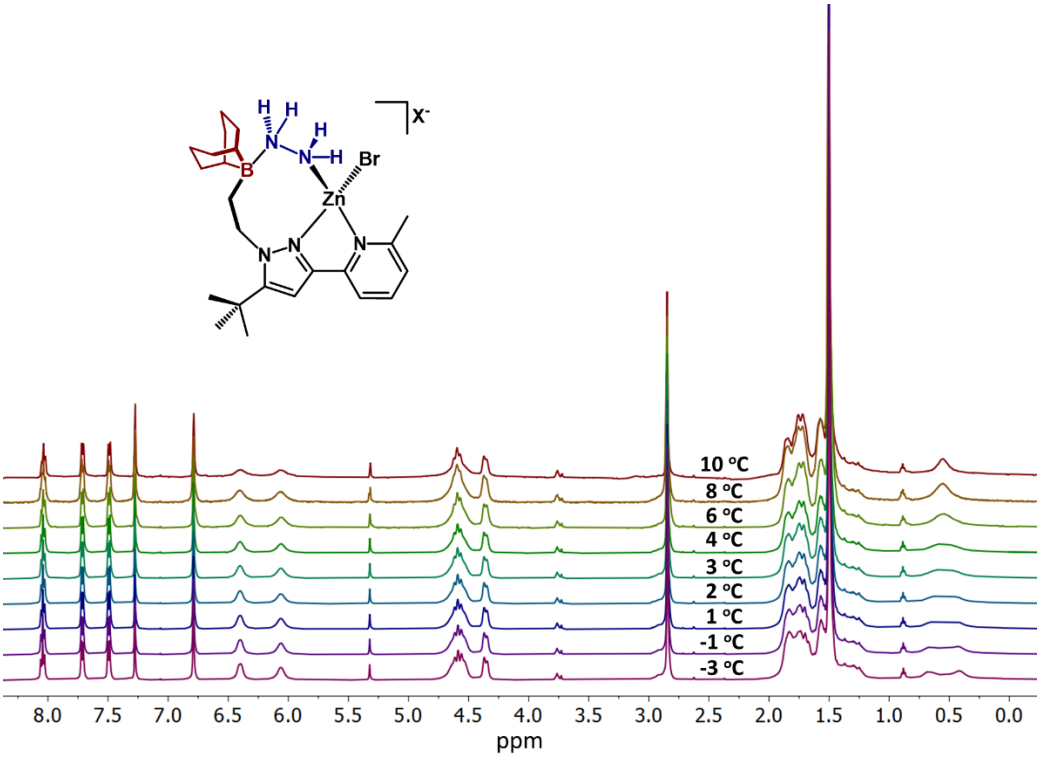


Figure S38 Variable temperature ^{1}H NMR spectra ($CDCl_3$) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range.

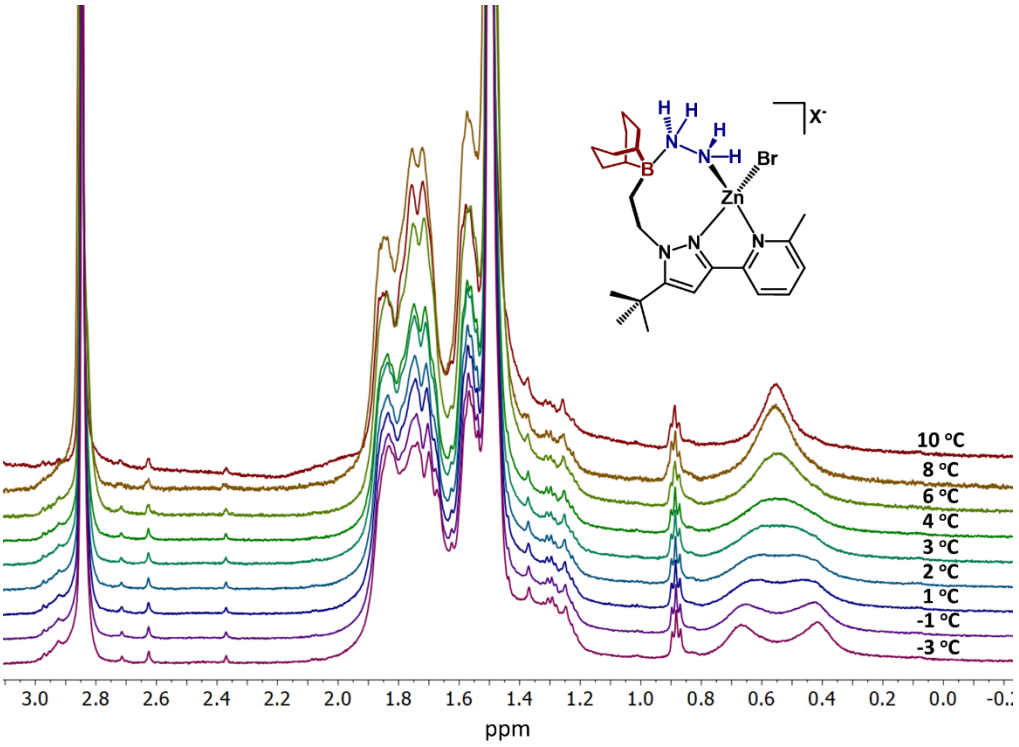


Figure S39 Variable temperature ^{1}H NMR spectra ($CDCl_3$) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range and zoomed to emphasize the upfield region.

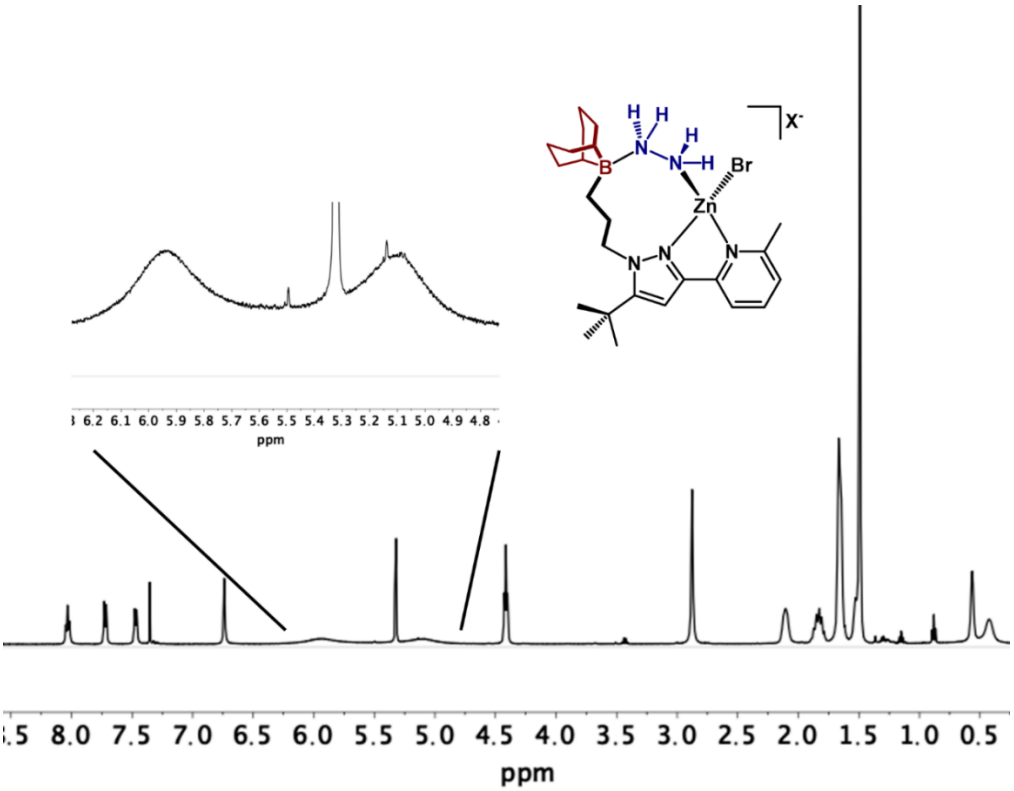


Figure S40 ^{1}H NMR spectrum (CD_2Cl_2, 25 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

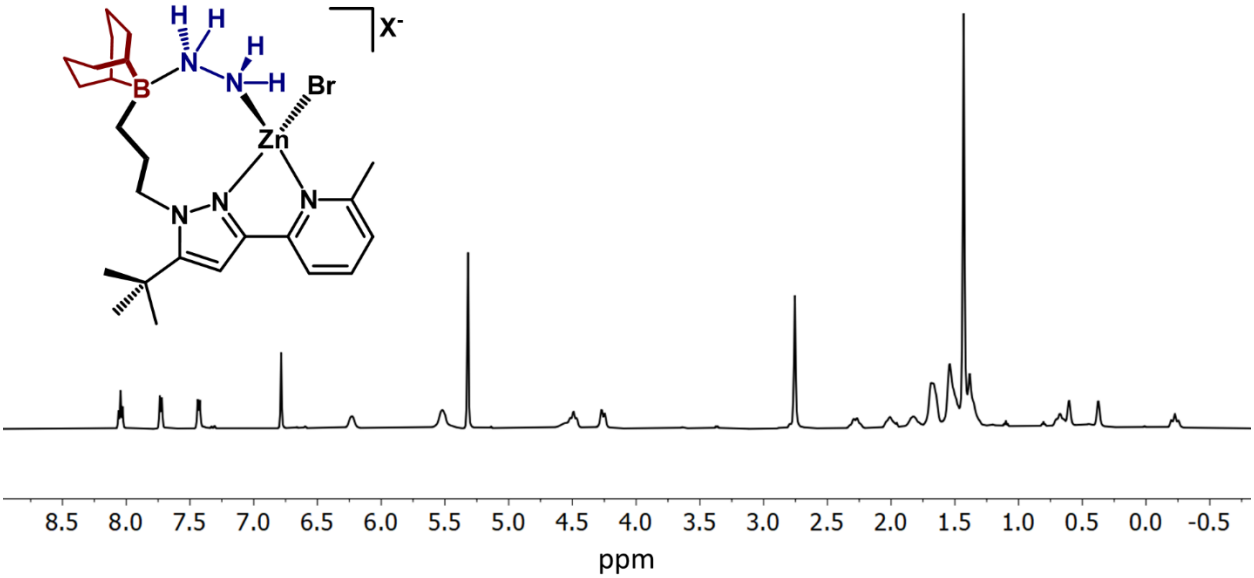


Figure S41 ^{1}H NMR spectrum (CD_2Cl_2, -60 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

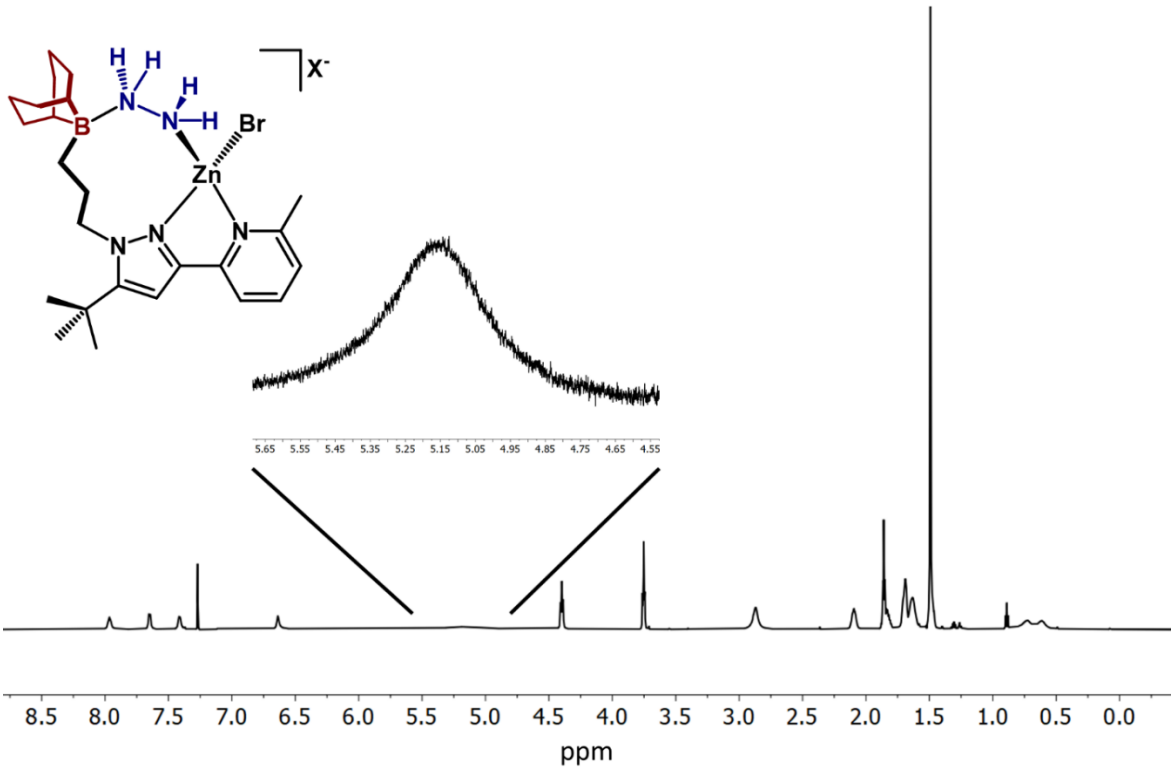


Figure S42 ^{1}H NMR spectrum ($CDCl_3$, 25 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

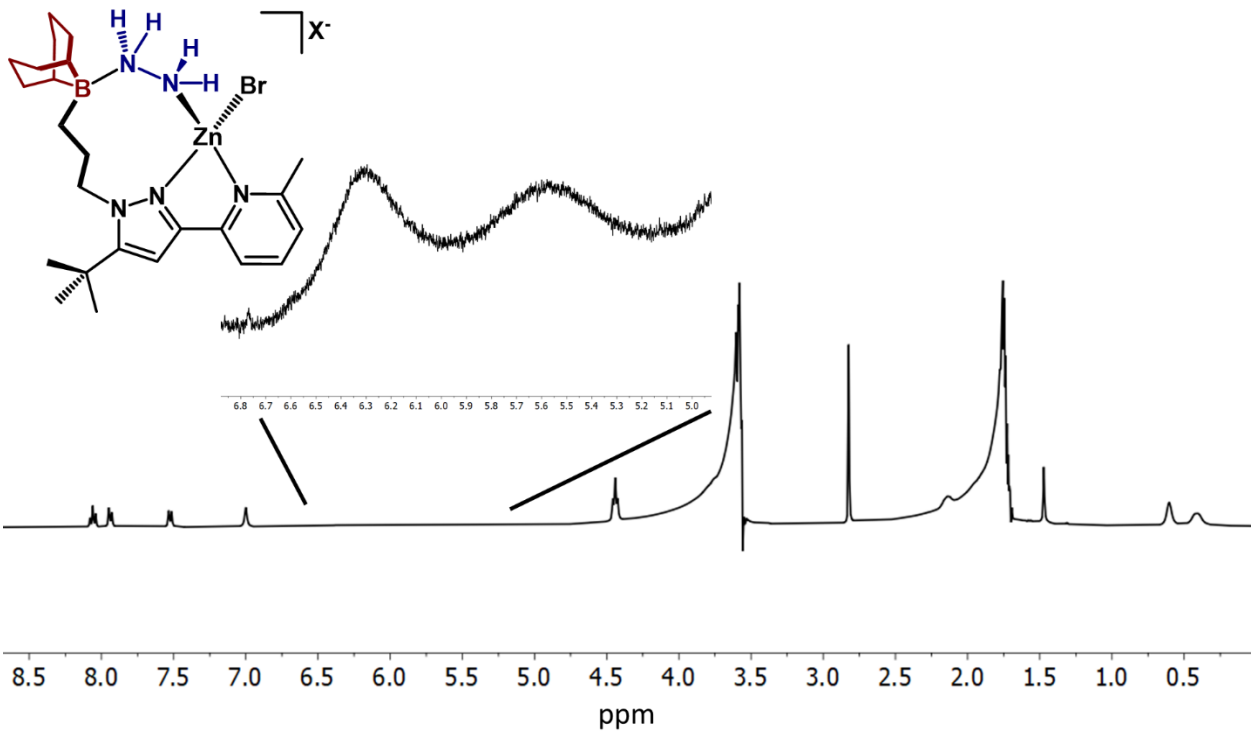


Figure S43 ^{1}H NMR spectrum (THF, 25 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

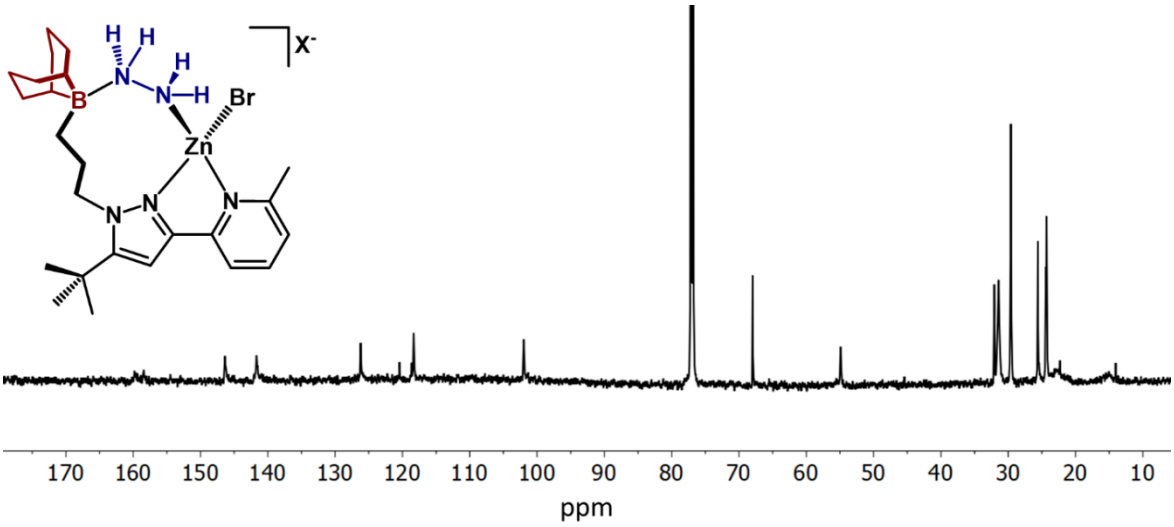


Figure S44 ^{13}C NMR spectrum ($CDCl_3$, 25 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

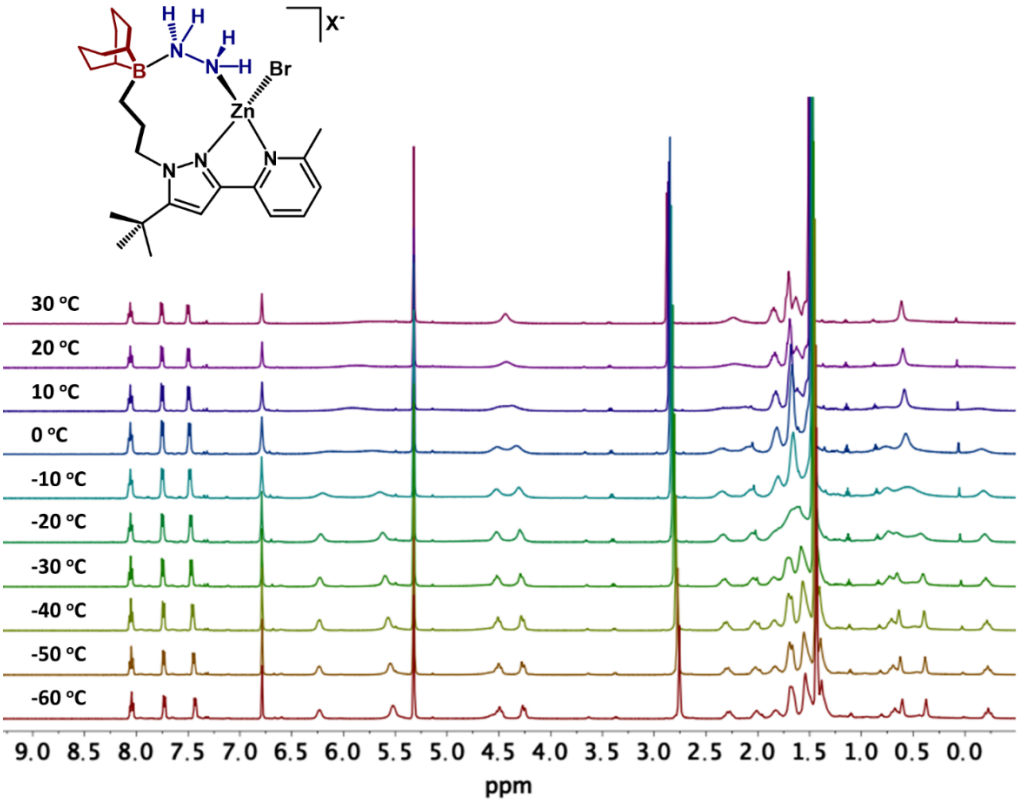


Figure S45 Variable temperature ^{1}H NMR spectrum (CD_2Cl_2) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

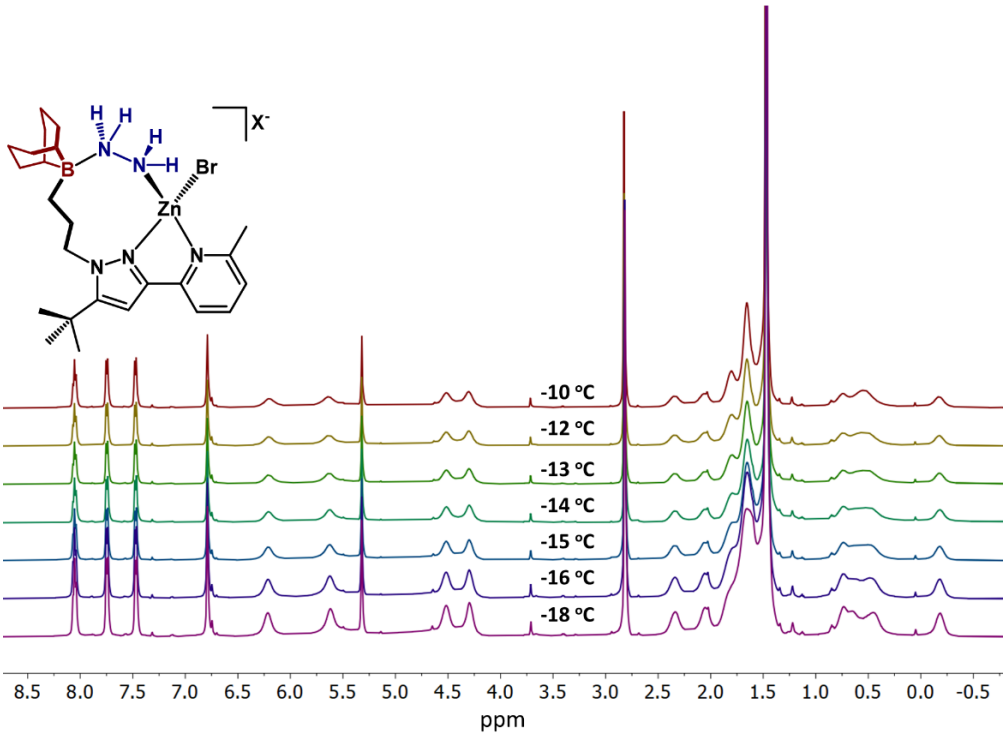


Figure S46 Variable temperature ^{1}H NMR spectrum (CD_2Cl_2) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range.

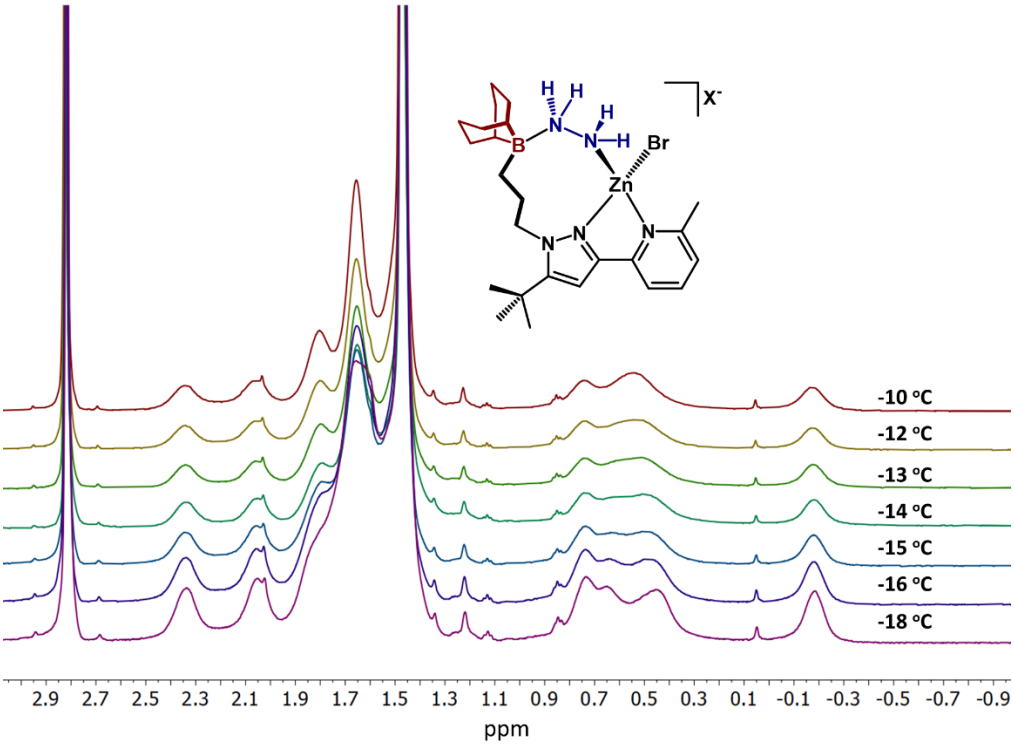


Figure S47 Variable temperature ^{1}H NMR spectrum (CD_2Cl_2) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range and zoomed into upfield region.

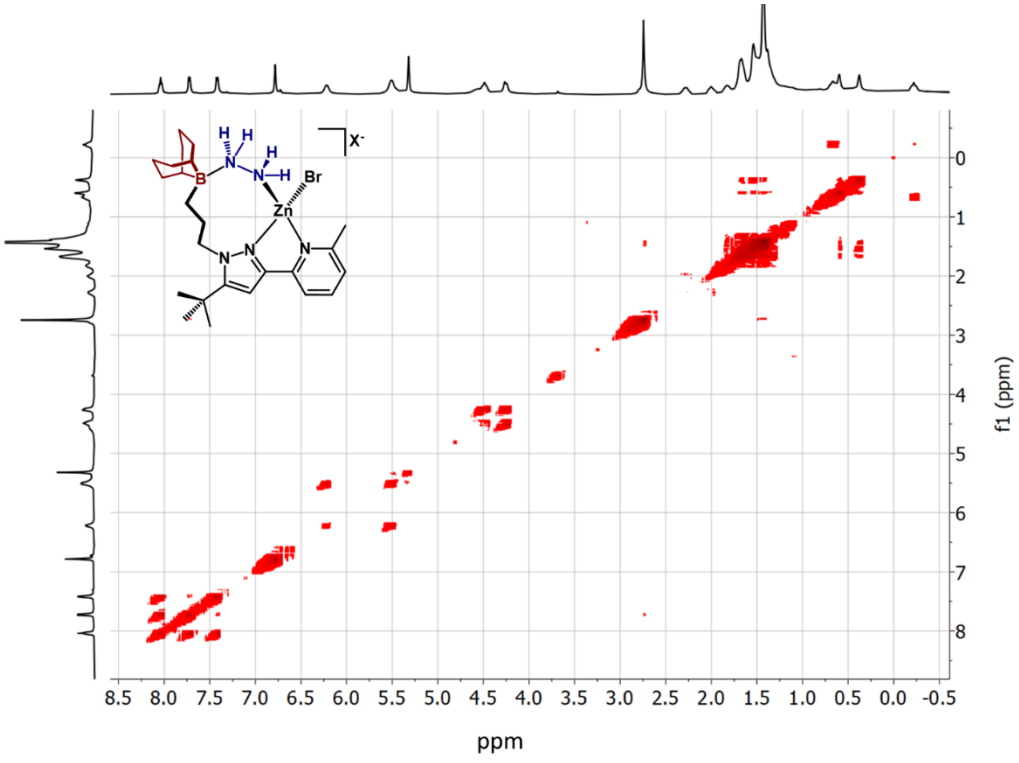


Figure S48 ^{1}H-^{1}H COSY spectrum (CD_2Cl_2, -60 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

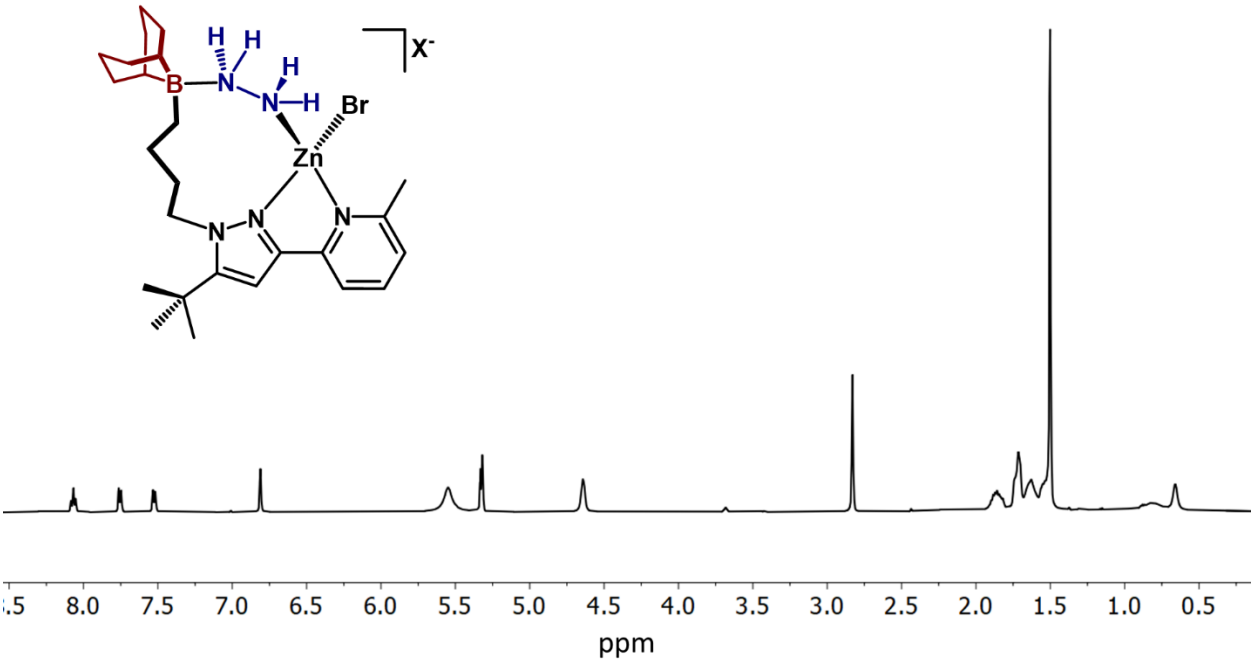


Figure S49 ^{1}H NMR spectrum (CD_2Cl_2, 25 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

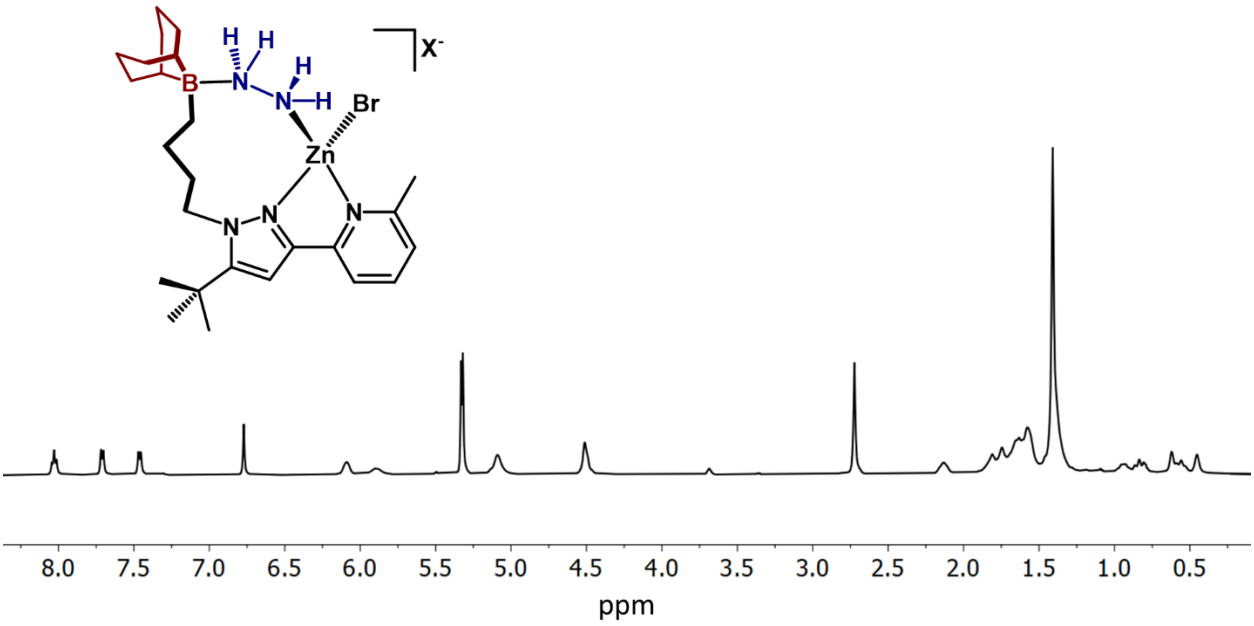


Figure S50 ^{1}H NMR spectrum (CD_2Cl_2, -75 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

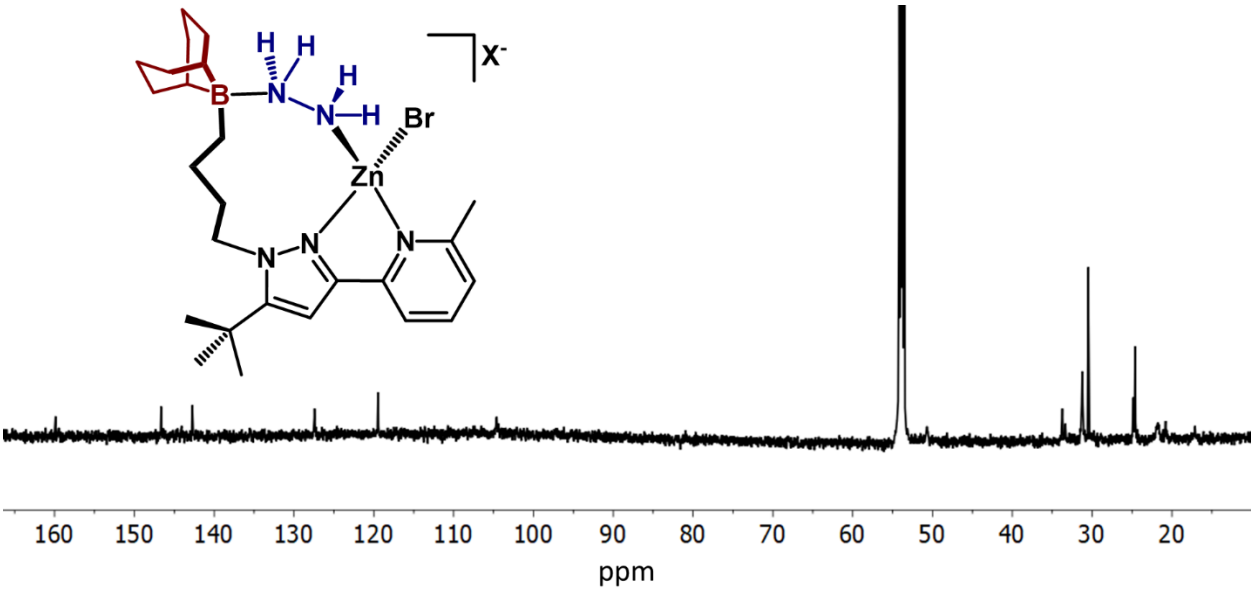


Figure S51 ^{13}C NMR spectrum (CD_2Cl_2, 25 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

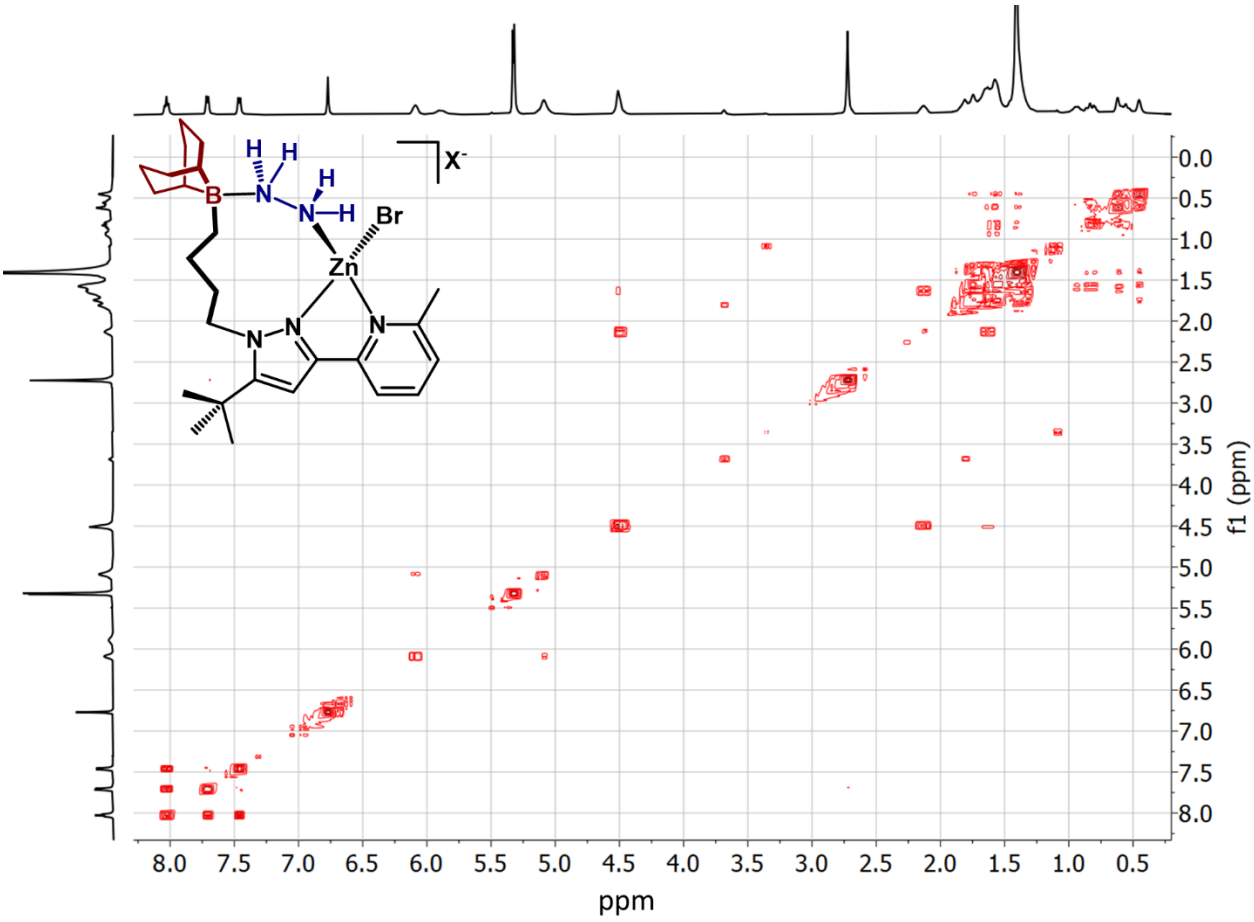


Figure S52 ^{1}H-^{1}H COSY spectrum (CD_2Cl_2, -75 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

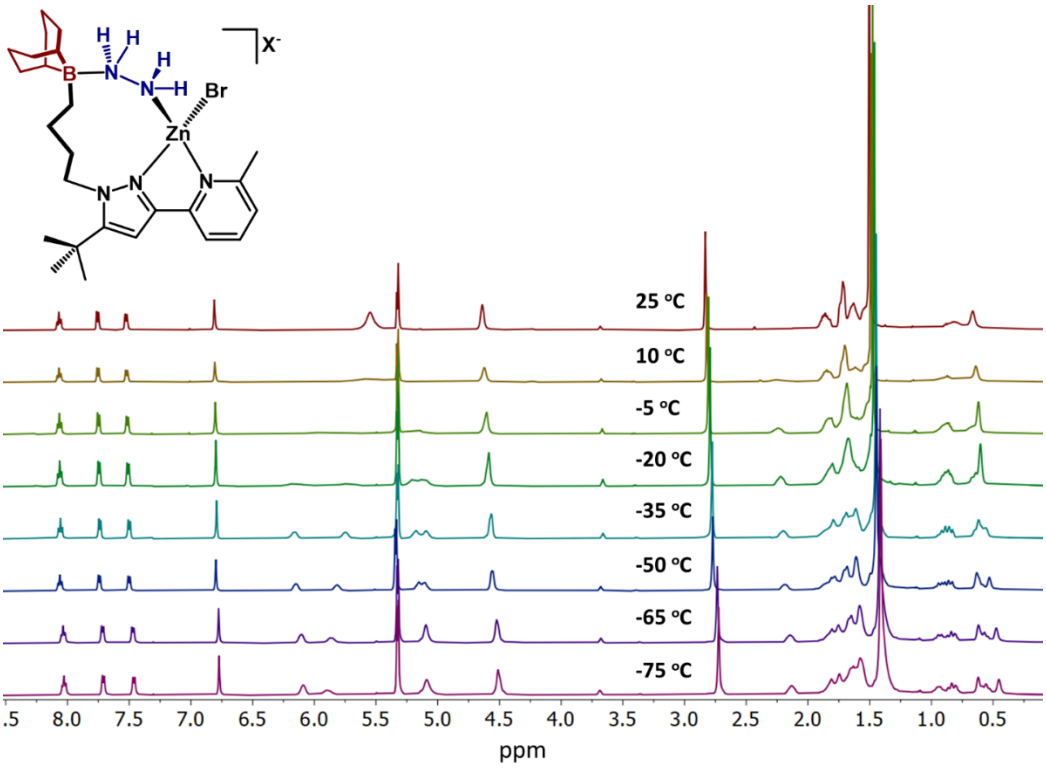


Figure S53 Variable temperature ^{1}H NMR spectra (CD_2Cl_2) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

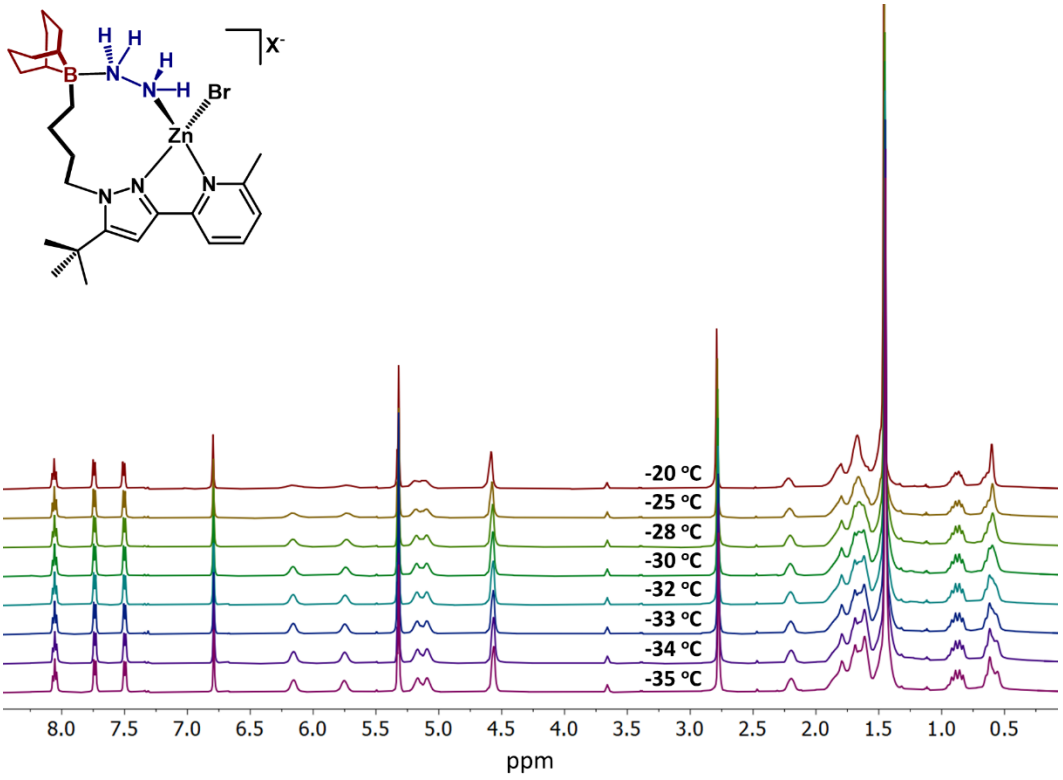


Figure S54 Variable temperature ^{1}H NMR spectra (CD_2Cl_2) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range.

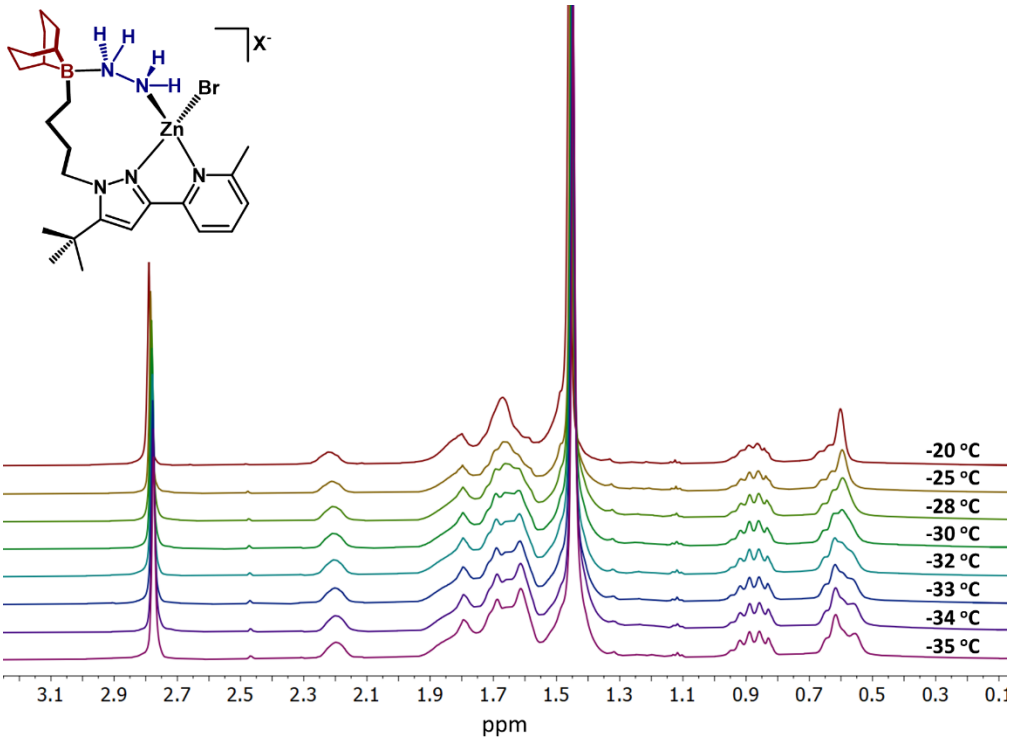


Figure S55 Variable temperature ^{1}H NMR spectra (CD_2Cl_2) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] over a more narrow temperature range and zoomed to emphasize upfield region.

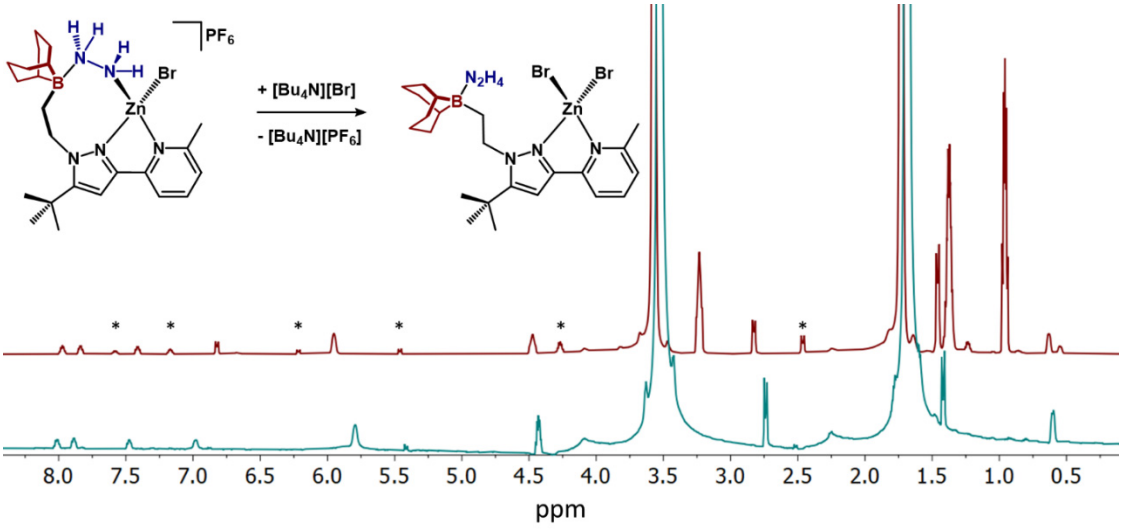


Figure S56 ^{1}H NMR spectra (THF, 25 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] prior to (bottom) and after addition of [Bu_4N][Br] (top) to form ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4). The asterisks are marking resonances associated to demetalation.

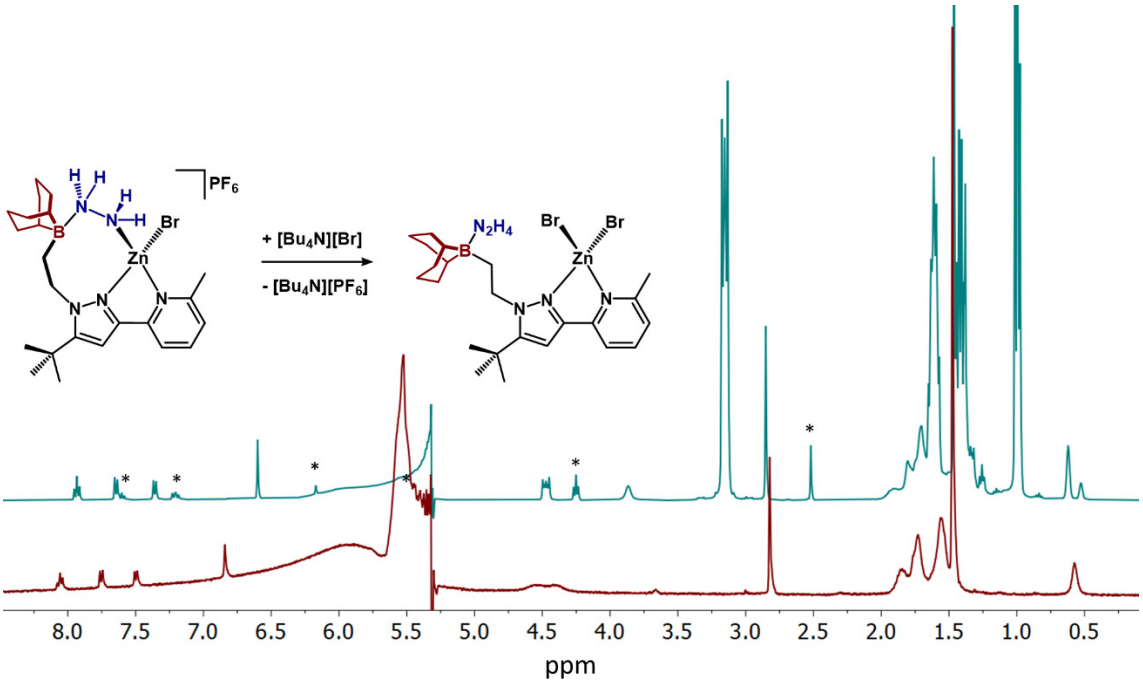


Figure S57 ^{1}H NMR spectra (DCM, 25 °C) of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] prior to (bottom) and after addition of [Bu_4N][Br] (top) to form ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4). The asterisks are marking resonances associated to demetalation.

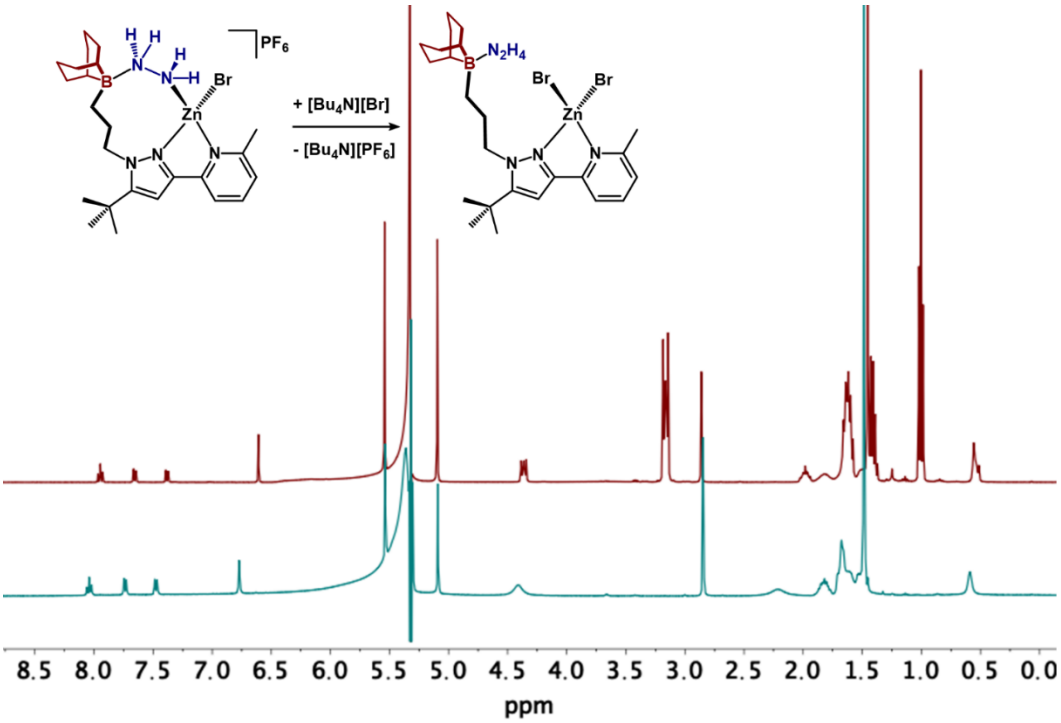


Figure S58 ^{1}H NMR spectra (DCM, 25 °C) of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] prior to (bottom) and after addition of [Bu_4N][Br] (top) to form ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4).

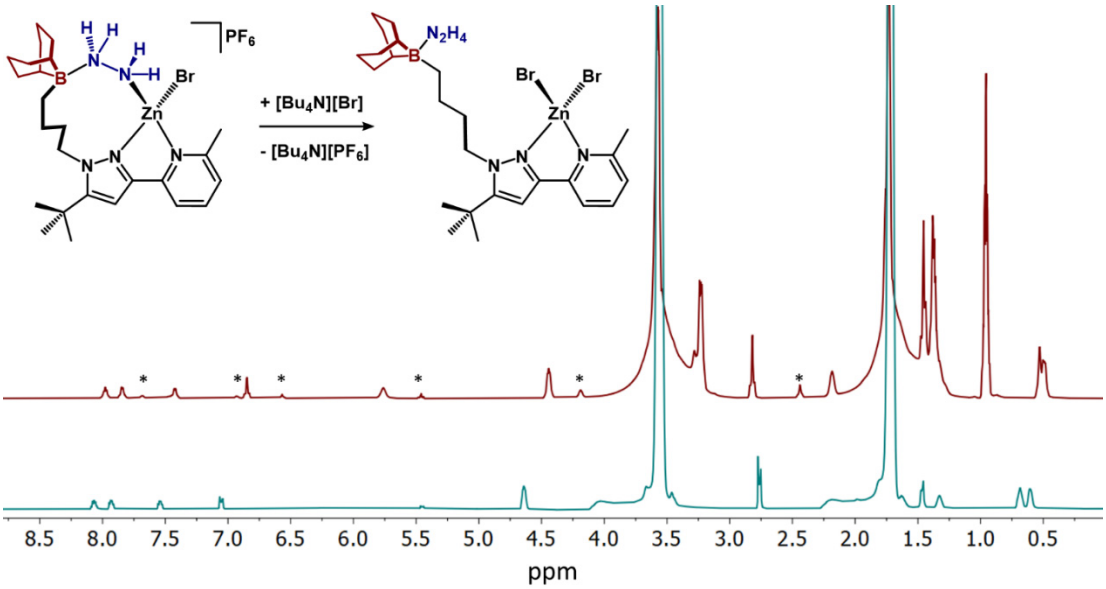


Figure S59 ^{1}H NMR spectra (THF, 25 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] prior to (bottom) and after addition of [Bu_4N][Br] (top) to form ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4). The asterisks are marking resonances associated to demetalation.

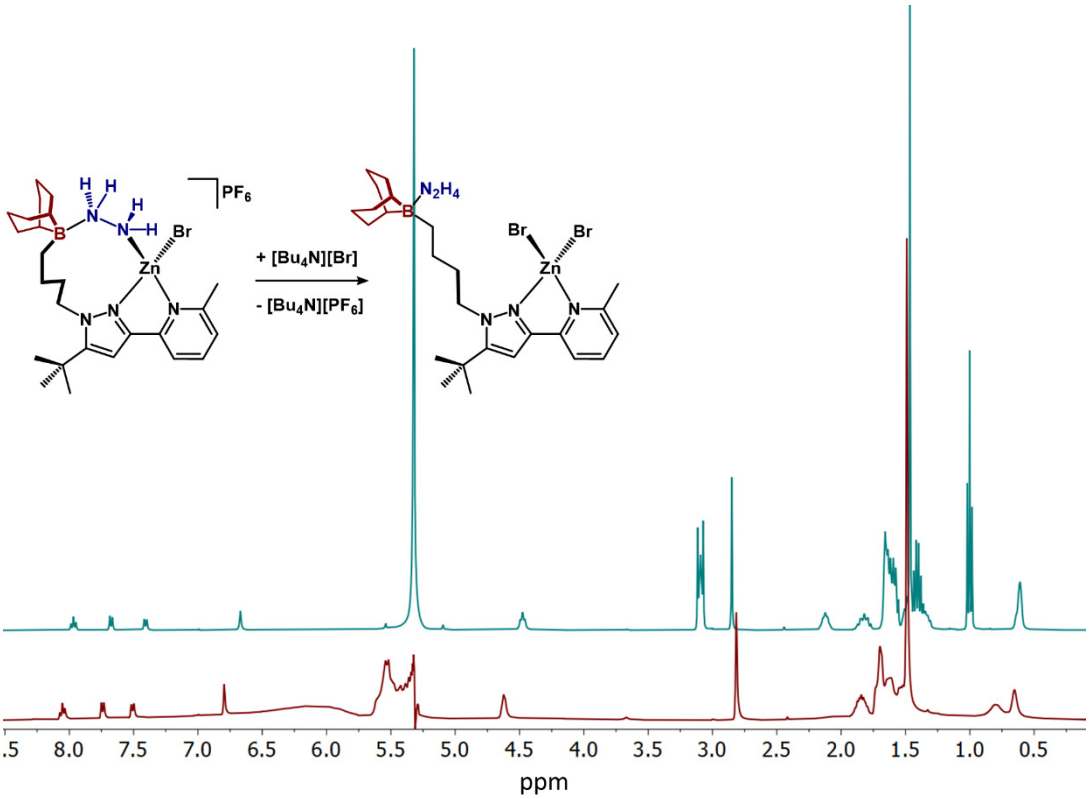


Figure S60 ^{1}H NMR spectra (THF, 25 °C) of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] prior to (bottom) and after addition of [Bu_4N][Br] (top) to form ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr_2(N_2H_4).

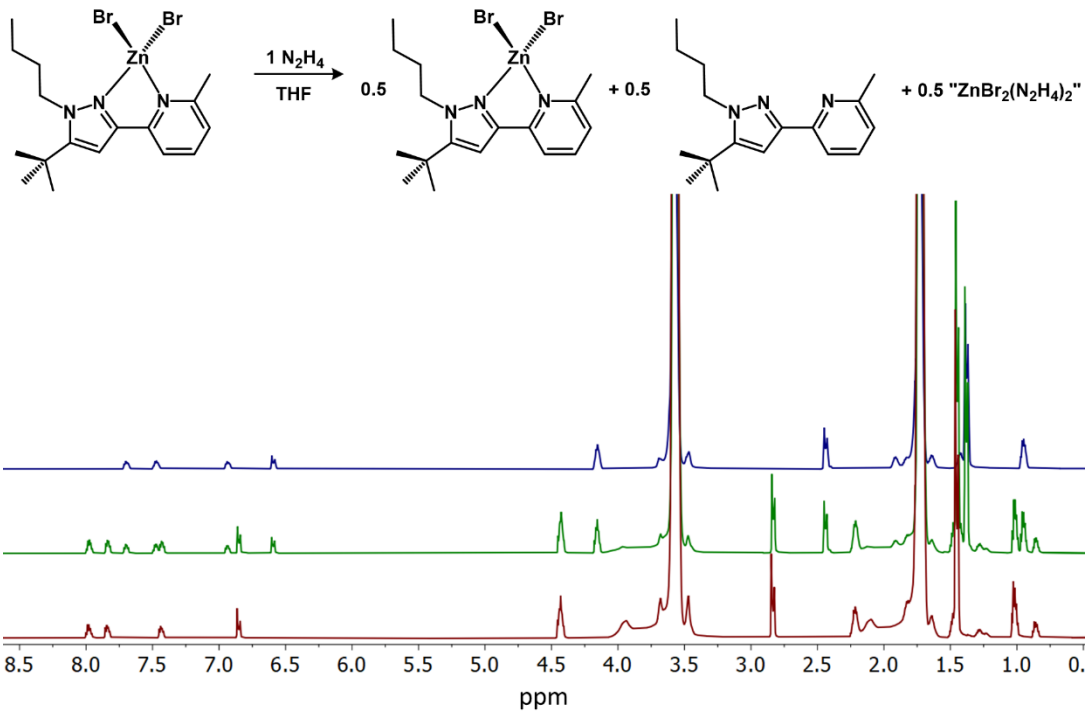


Figure S61 ^{1}H NMR spectra (THF, 25 °C) of (^{butyl}NN^{tBu})ZnBr$_2$ prior to (bottom) and after addition of one equivalent of N_2H_4. The ^{1}H NMR spectrum of the free ligand, ^{butyl}NN^{tBu}, is also provided (top).

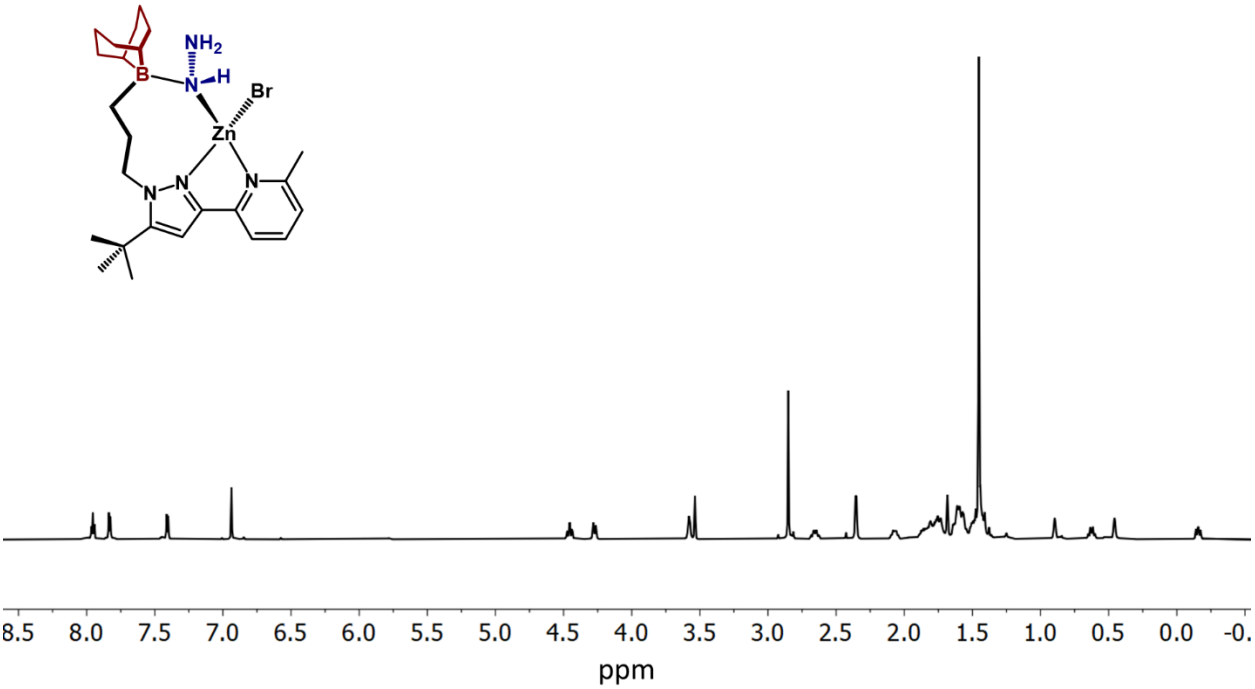


Figure S62 ^{1}H NMR spectrum (THF-d_8, 25 °C) of ($^{3\text{-BBN}}$NN^{tBu})ZnBr(N_2H_3).

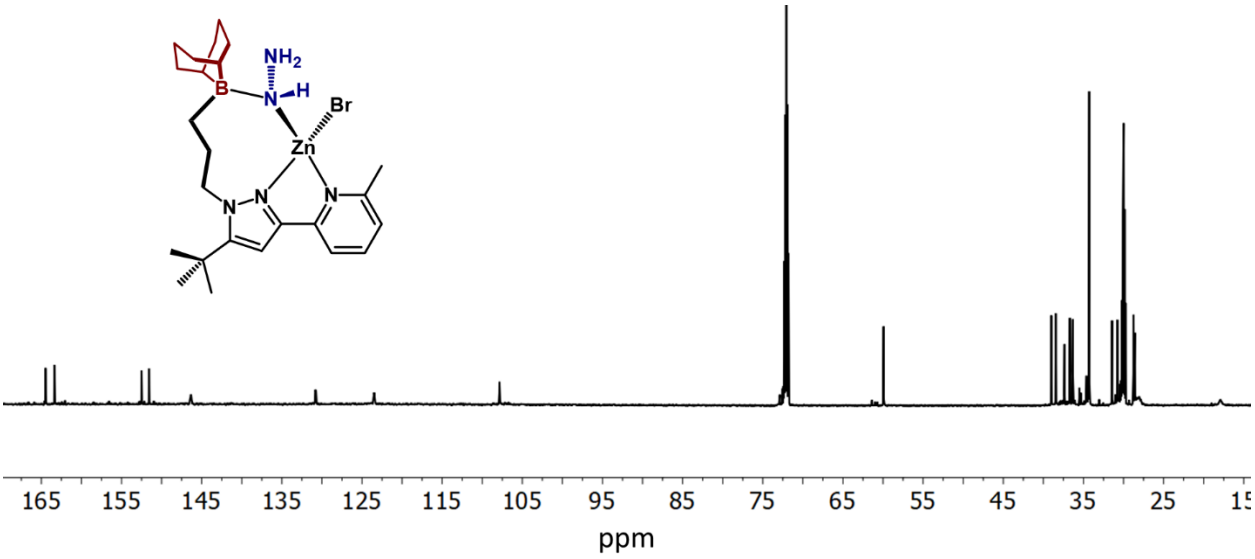


Figure S63 ^{13}C NMR spectrum (THF-d_8, 25 °C) of ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3).

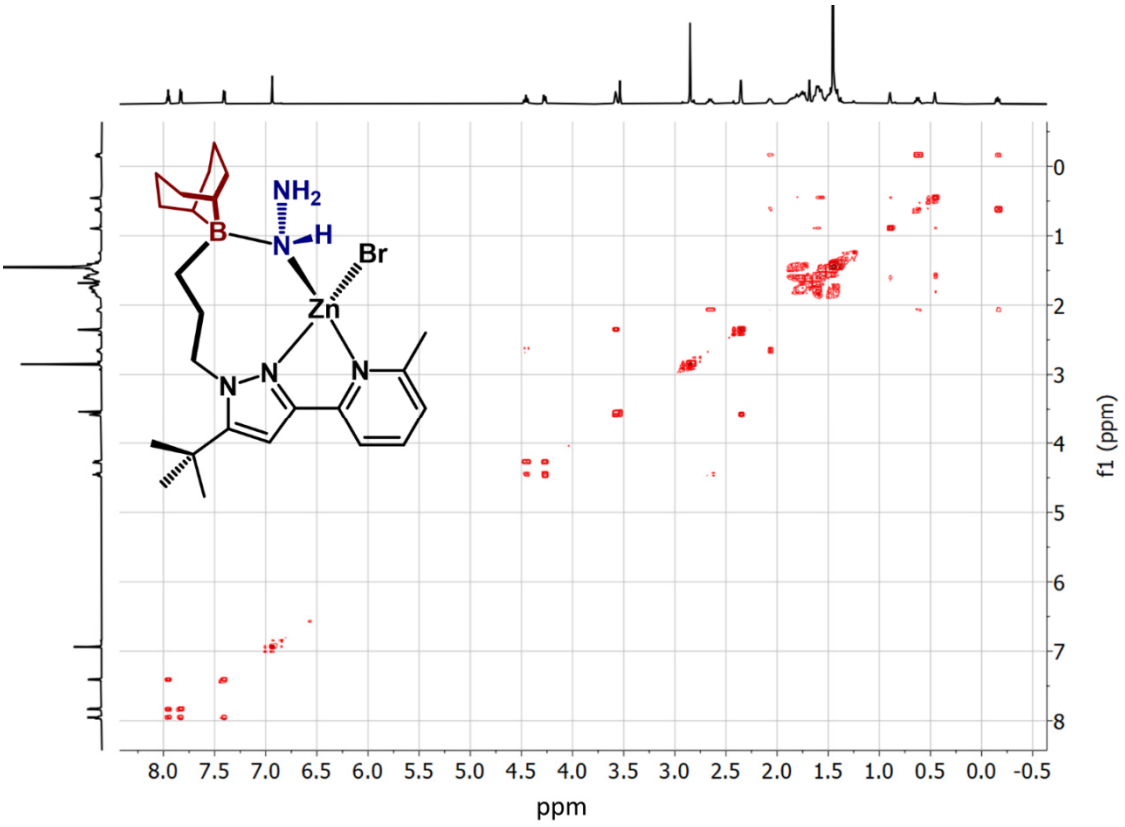


Figure S64 ^{1}H-^{1}H COSY spectrum (THF-d_8, 25 °C) of ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3).

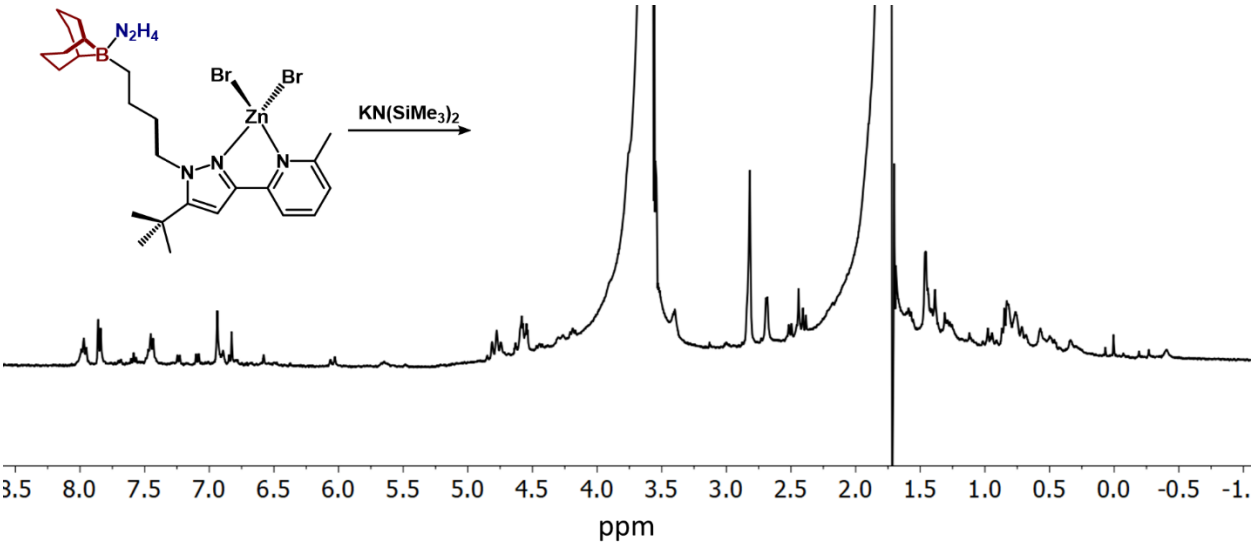


Figure S65 ^{1}H NMR spectrum (THF, 25 °C) of attempted formation of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3). See experimental section for details.

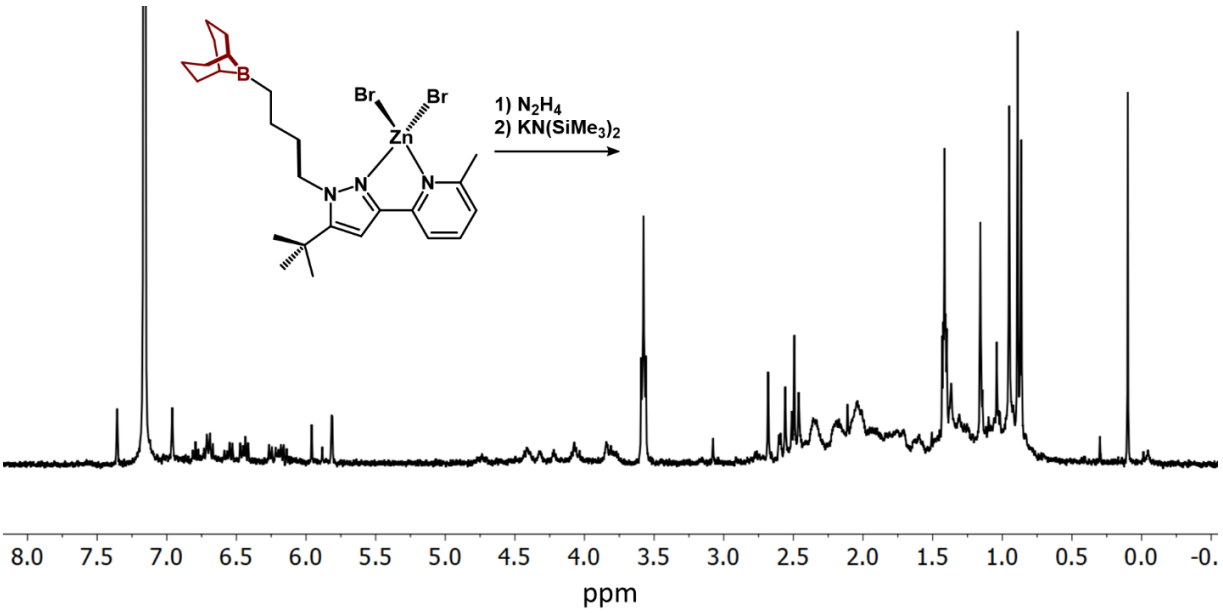


Figure S66 ^{1}H NMR spectrum (C_6D_6, 25 °C) of attempted formation of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3). See experimental section for details.

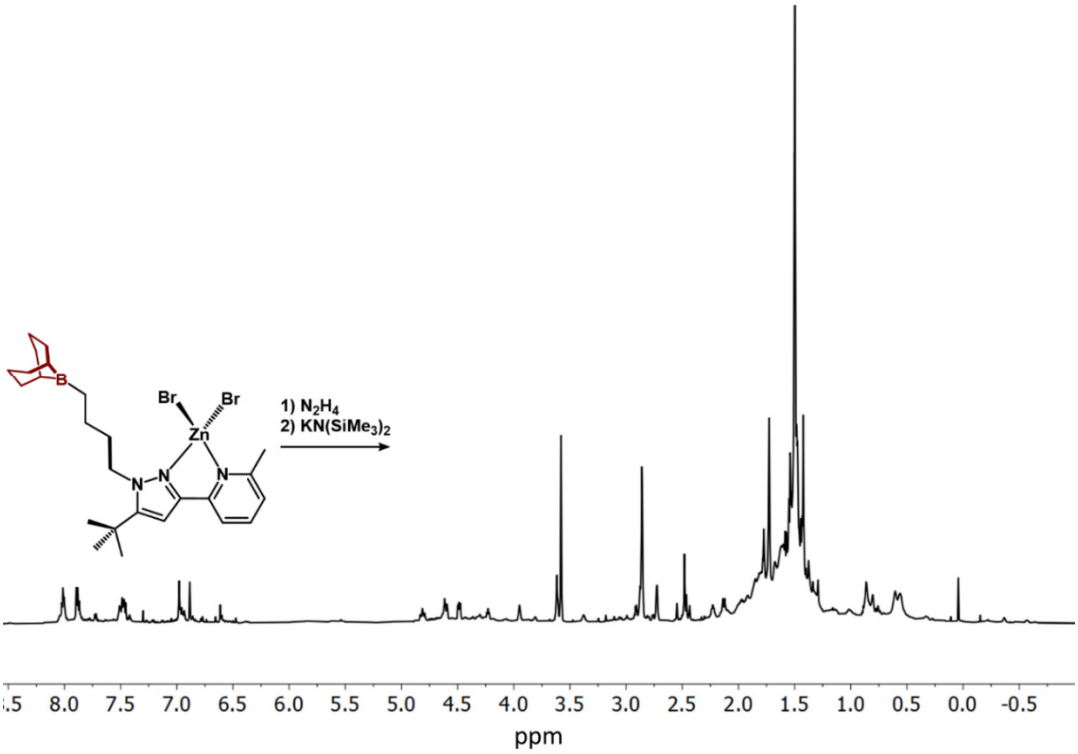


Figure S67 ^{1}H NMR spectrum (C_6D_6, 25 °C) of attempted formation of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3). See experimental section for details.

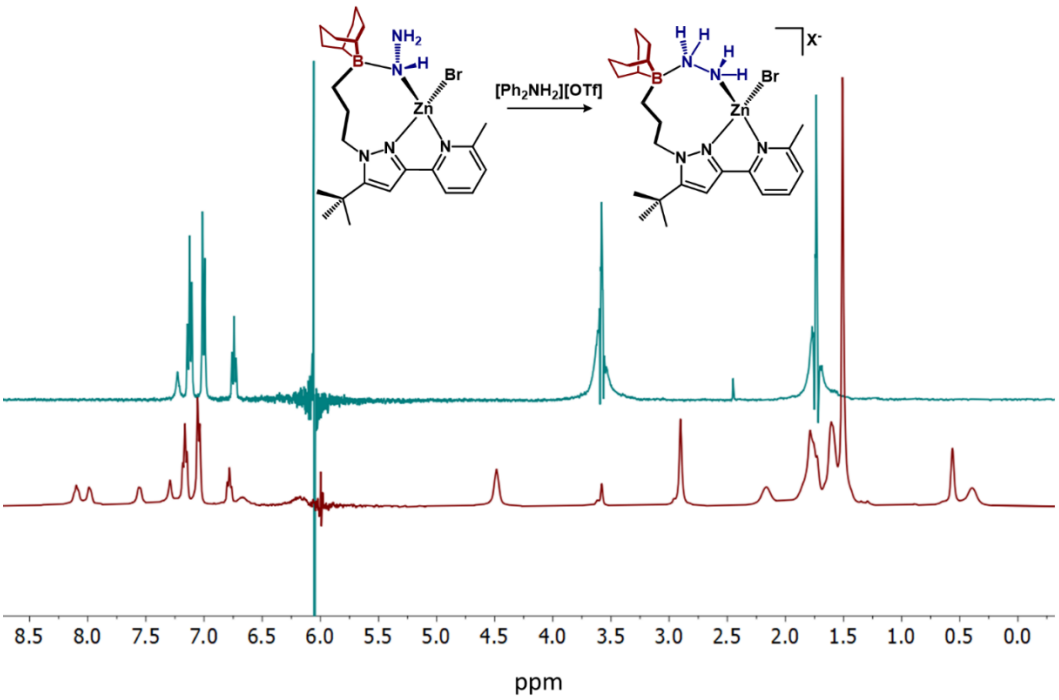


Figure S68 Bottom: ^{1}H NMR spectrum (THF-d_8, 25 °C) of crude reaction of protonation of ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3) with $[Ph_2NH_2][OTf]$. Top: ^{1}H NMR spectrum of diphenylamine (THF, 25 °C) for comparison.

Determination of $\Delta G^{\ddagger}$ and k_c for $[(^{n\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$

The equation used to estimate $\Delta G^{\ddagger}$ using the coalescence temperature is:

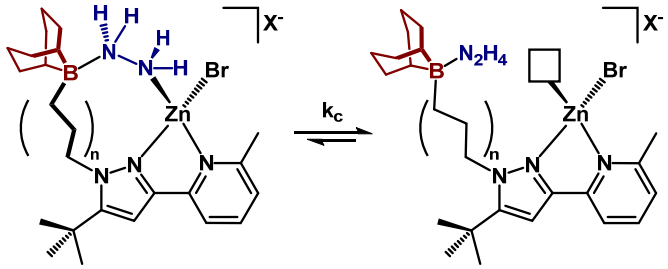
$\Delta G^{\ddagger} = aT_c[9.972 + \log(T_c/\Delta v)]$

Where $a = 4.575 \times 10^{-3}$ kcal/mol

T_c = experimentally determined coalescence temperature (K)

Δv = maximum peak separation (Hz) in the low-temperature limit.

At the coalescence temperature, $k_c = \pi(\Delta v)/\sqrt{2}$



	solvent	$\Delta\nu$ (Hz)	T_c (K)	k_c (s^{-1})	$\Delta G^{\ddagger}$ (kcal/mol)
2-BBN	$CDCl_3$	168.6 (223 K)	276	375	12.8 (+/- 0.1)
3-BBN	CD_2Cl_2	110.0 (213 K)	260	244	12.3 (+/- 0.1)
4-BBN	CD_2Cl_2	83.2 (198 K)	240	185	11.5 (+/- 0.2)

Figure S69 Parameters extracted from VT-NMR data.

Notes

2-BBN: For the analysis, the resonances attributed to B-C*H* were used. For these resonances, at -50 °C, in $CDCl_3$, δ = 0.31 (s, 1H, B-C*H*), 0.64 (s, 1H, B-C*H*). The variable temperature profile of these resonances is well resolved and do not overlap with other resonances at the coalescence temperature. The value for Δv shows minimal variation for the two coldest temperatures recorded ($\Delta\Delta v$ = 7.1 Hz from -35 and -50 °C). These data suggest at -50 °C, in $CDCl_3$, the molecule is near the slow-exchange limit and the error associated with the extracted parameters are likely minimal.

3-BBN: For the analysis, the resonances attributed to B-C*H* were used. For these resonances, at -60 °C, in CD_2Cl_2, δ = 0.37 (s, 1H, B-C*H*), 0.60 (s, 1H, B-C*H*). The variable temperature profile of these resonances is relatively well resolved despite partial overlap with another resonance near the coalescence temperature. The value for Δv shows minimal variation for the two coldest temperatures recorded ($\Delta\Delta v$ = 4.7 Hz from -50 and -60 °C). These data suggest at -60 °C, in CD_2Cl_2, the molecule is near the slow-exchange limit and the error associated with the extracted parameters are likely minimal.

4-BBN: For the analysis, the resonances attributed to B-C*H* were used. For these resonances, at -75 °C, in CD_2Cl_2, δ = 0.45 (s, 1H, B-C*H*), 0.62 (s, 1H, B-C*H*). The variable temperature profile of these resonances is not well resolved from other overlapping resonances. We interpret the data as providing a coalescence temperature of 240 K (-33 °C). Due to overlap, this temperature may range 239-241 K. These temperature discrepancies will not greatly affect the extracted $\Delta G^{\ddagger}$ value (+/- 0.1 kcal/mol). However, the value for Δv shows variation for the two coldest temperatures recorded ($\Delta\Delta v$ = 11.6 Hz from -65 and -75 °C). These data suggest at -75 °C, in CD_2Cl_2, the molecule may not have reached the slow-exchange limit. Therefore, the extracted rate, 185 s^{-1}, should be viewed as a minimum estimate.

Complex: (^{vinyl}NN^{tBu})ZnBr$_2$

Local name: ML183

CCDC: 2012063

Table S1 Experimental parameters for (^{vinyl}NN^{tBu})ZnBr$_2$.

Crystal data	
Chemical formula	$C_{15}H_{19}Br_2N_3Zn$
M_r	466.52
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	13.6806 (8), 9.1444 (4), 14.0282 (8)
β (°)	100.311 (2)
V (Å^3)	1726.60 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.05
Crystal size (mm)	0.19 × 0.15 × 0.05
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.596, 0.746
No. of measured, independent and observed [I > 2s(I)] reflections	25393, 5157, 3247
R_{int}	0.075
(sin θ/λ)$_{max}$ (Å^{-1})	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.043, 0.082, 1.00
No. of reflections	5157
No. of parameters	194
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.77, -0.66

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev988 (Hübschle *et al.*, 2011).

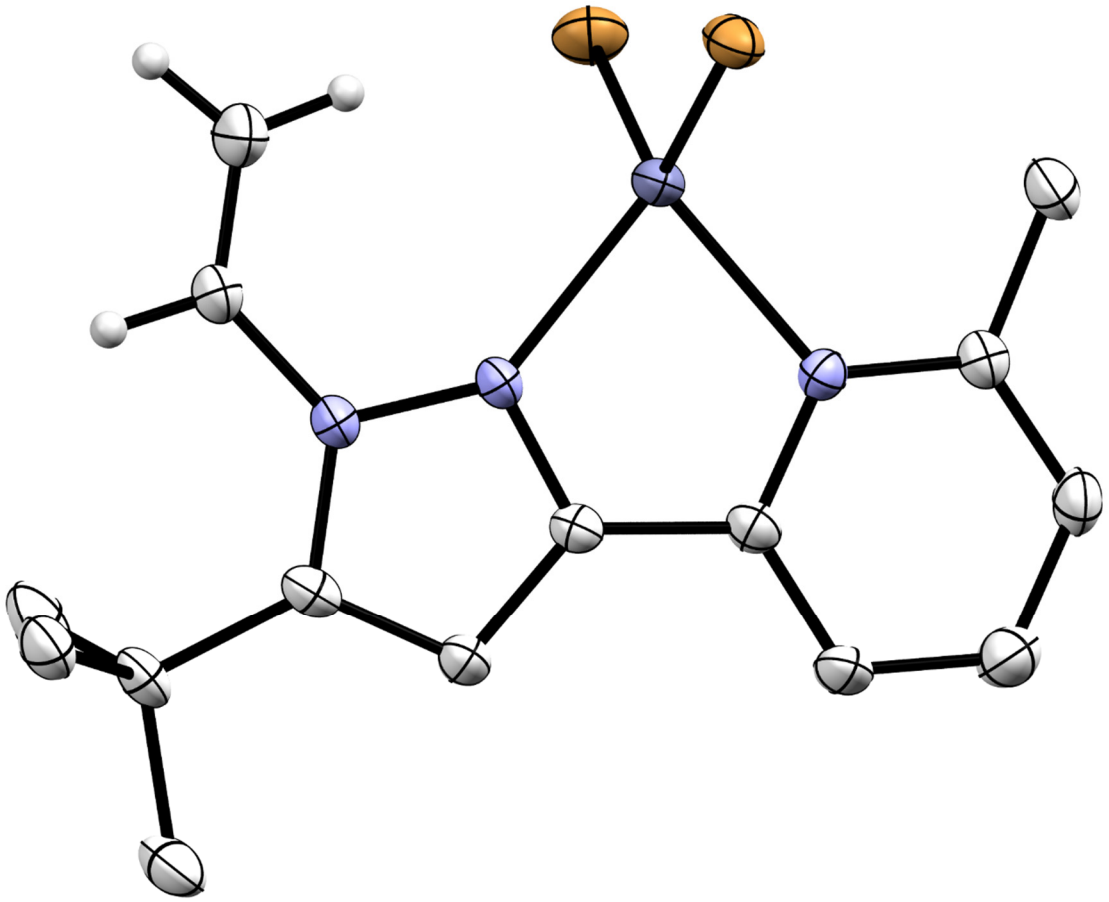


Figure S70 Molecular structure of (^{vinyl}NN^{tBu})ZnBr$_2$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to vinyl moiety are omitted for clarity.

Complex: (^{butene}NN^{tBu})ZnBr$_2$

Local name: JK5218

CCDC: 2012067

Table S2 Experimental parameters for (^{butene}NN^{tBu})ZnBr$_2$.

Crystal data	
Chemical formula	$C_{17}H_{23}Br_2N_3Zn$
M_r	494.57
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	17.2348 (11), 11.4411 (8), 20.0805 (14)
β (°)	92.729 (3)
V (Å^3)	3955.1 (5)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.29
Crystal size (mm)	0.55 × 0.53 × 0.45
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.113, 0.269
No. of measured, independent and observed [I > 2s(I)] reflections	68979, 12069, 8374
R_{int}	0.072
(sin θ/λ)$_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.126, 1.04
No. of reflections	12069
No. of parameters	424
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.38, -1.08

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev988 (Hübschle *et al.*, 2011).

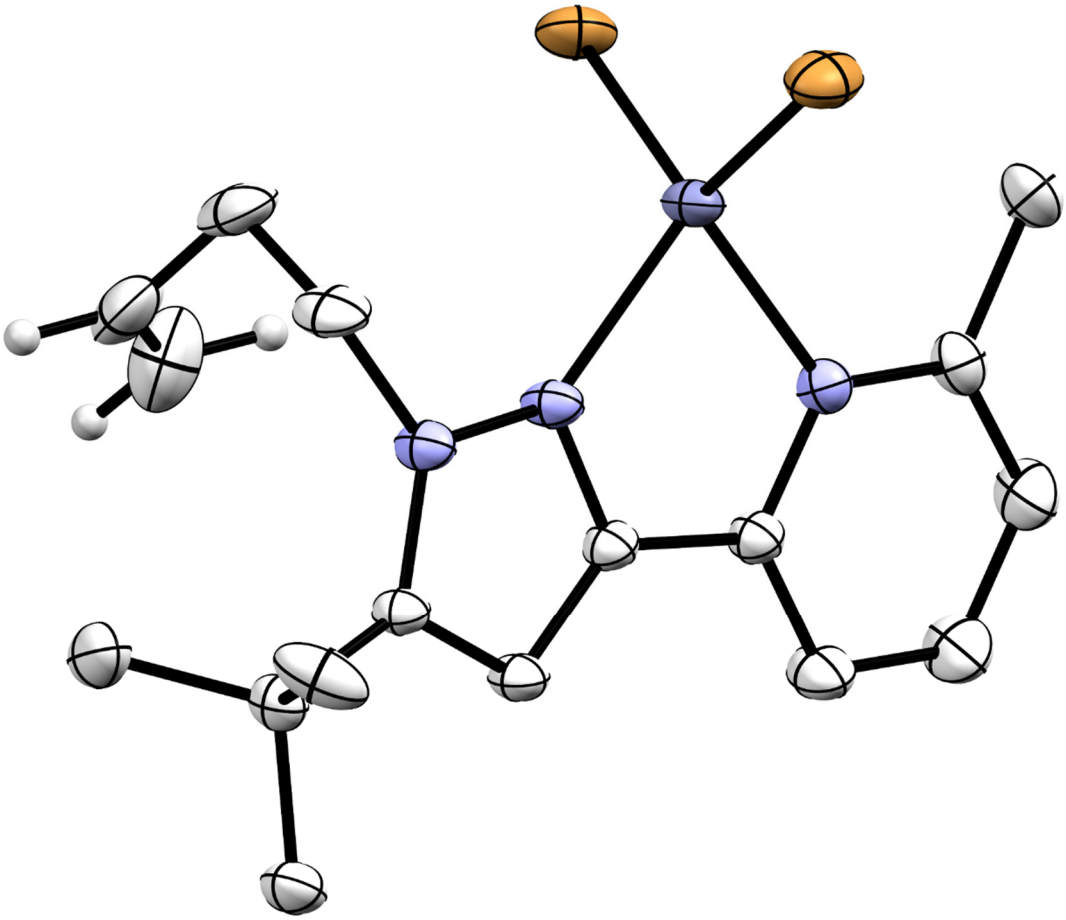


Figure S71 Molecular structure of (^{butene}NN^{tBu})ZnBr$_2$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to alkene moiety are omitted for clarity.

Complex: (^{butyl}NN^{tBu})ZnBr$_2$

Local name: JK5217

CCDC: 2012064

Table S3 Experimental parameters for (^{butyl}NN^{tBu})ZnBr$_2$.

Crystal data	
Chemical formula	$C_{17}H_{25}Br_2N_3Zn$
M_r	496.59
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	12.8681 (6), 11.5859 (5), 14.3384 (8)
β (°)	103.984 (2)
V (Å^3)	2074.34 (18)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.04
Crystal size (mm)	0.55 × 0.45 × 0.06
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.437, 0.747
No. of measured, independent and observed [I > 2s(I)] reflections	32067, 7525, 4618
R_{int}	0.061
(sin θ/λ)$_{max}$ (Å^{-1})	0.770
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.152, 0.95
No. of reflections	7525
No. of parameters	213
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.24, -1.20

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev988 (Hübschle *et al.*, 2011).

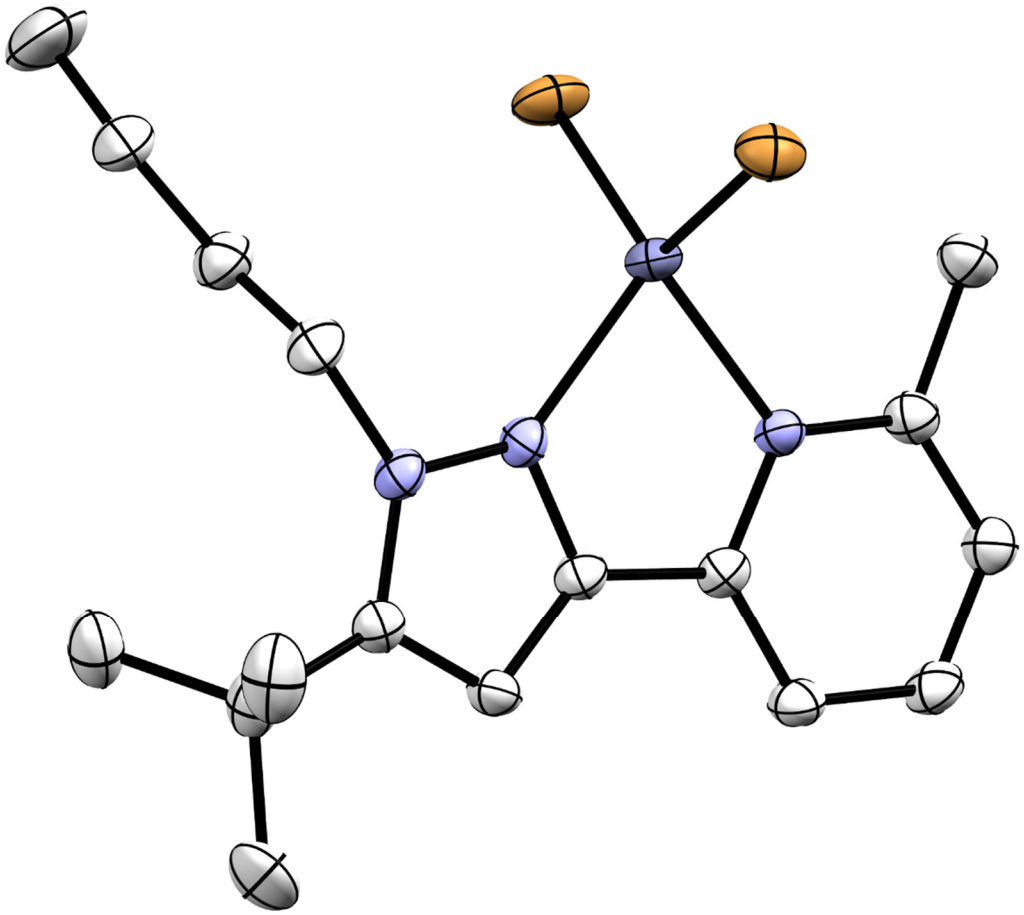


Figure S72 Molecular structure of (^{butyl}NN^{tBu})ZnBr$_2$ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Complex: ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2$

Local name: ML141

CCDC: 2012065

Table S4 Experimental parameters for ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2$.

Crystal data	
Chemical formula	$C_{23}H_{34}BBr_2N_3Zn$
M_r	588.53
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	13.0034 (9), 13.5104 (10), 15.0119 (14)
α, β, γ (°)	86.957 (3), 87.514 (4), 73.838 (4)
V (Å^3)	2528.4 (4)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	4.15
Crystal size (mm)	0.13 × 0.12 × 0.07
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.553, 0.746
No. of measured, independent and observed [$I > 2s(I)$] reflections	47737, 12294, 9973
R_{int}	0.040
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.102, 1.08
No. of reflections	12294
No. of parameters	549
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.79, -1.50

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

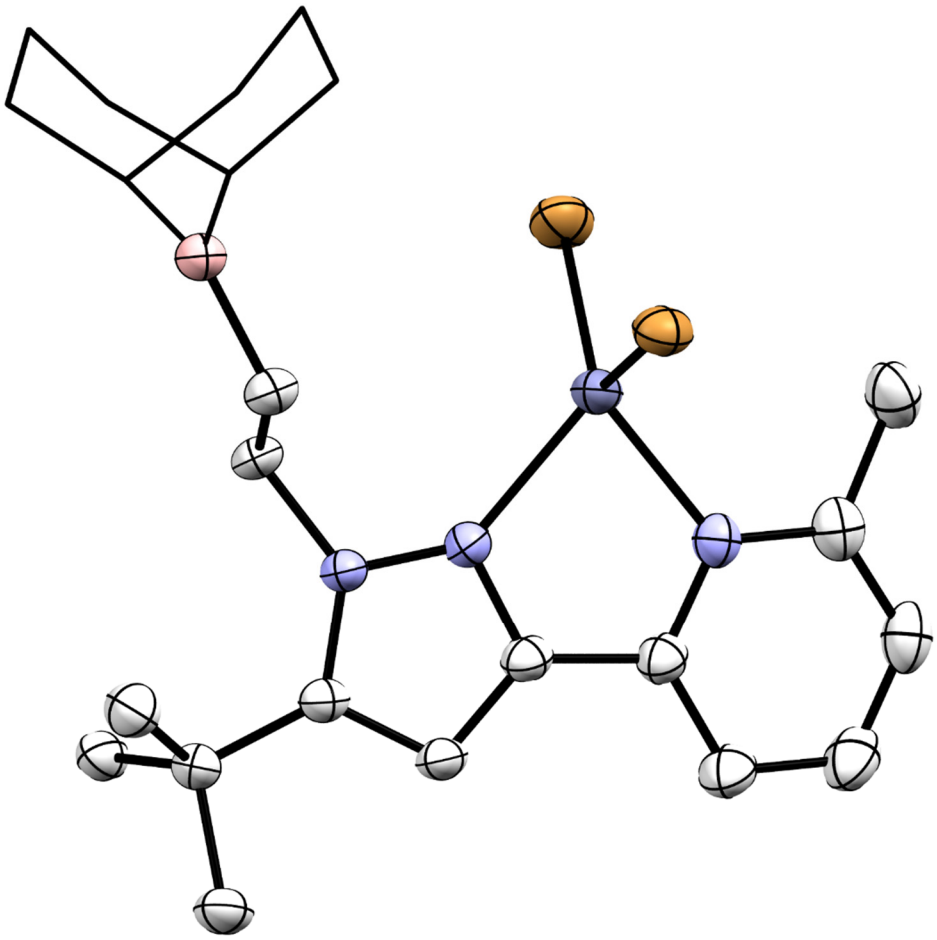


Figure S73 Molecular structure of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity.

Complex: ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2$

Local name: JK5219

CCDC: 2012070

Table S5 Experimental parameters for ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2$.

Crystal data	
Chemical formula	$C_{25}H_{38}BBr_2N_3Zn$
M_r	616.58
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	15.0468 (16), 11.2801 (7), 16.7588 (17)
β (°)	103.198 (2)
V (Å^3)	2769.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.79
Crystal size (mm)	0.22 × 0.11 × 0.07
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.469, 0.746
No. of measured, independent and observed [I > 2s(I)] reflections	25468, 7432, 5650
R_{int}	0.059
(sin θ/λ)$_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.106, 1.04
No. of reflections	7432
No. of parameters	366
No. of restraints	341
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, -0.88

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev988 (Hübschle *et al.*, 2011).

Refinement details:

The 9-BBN fragment is disordered. The two disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.749(4) to 0.251(4).

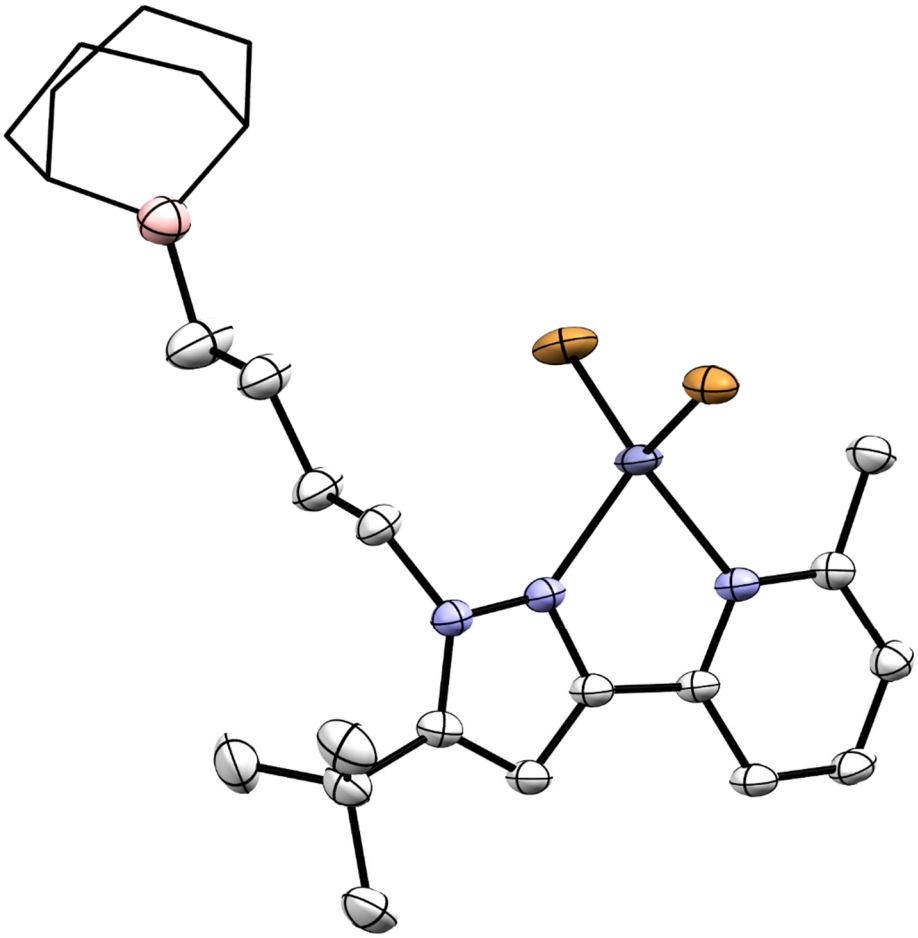


Figure S74 Molecular structure of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2$ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe and only the major disordered moiety is shown for improved clarity.

Complex: ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$

Local name: ML73_2

CCDC: 2012066

Table S6 Experimental parameters for ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{23}H_{38}BBr_2N_5Zn \cdot C_6H_6$
M_r	698.69
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	10.6610 (5), 11.8149 (6), 13.2704 (6)
α, β, γ (°)	105.494 (2), 99.734 (2), 101.500 (2)
V (Å^3)	1534.07 (13)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	3.43
Crystal size (mm)	0.21 × 0.17 × 0.12
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.634, 0.747
No. of measured, independent and observed [$I > 2s(I)$] reflections	46054, 11627, 7716
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.079, 1.01
No. of reflections	11627
No. of parameters	359
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.07, -0.81

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

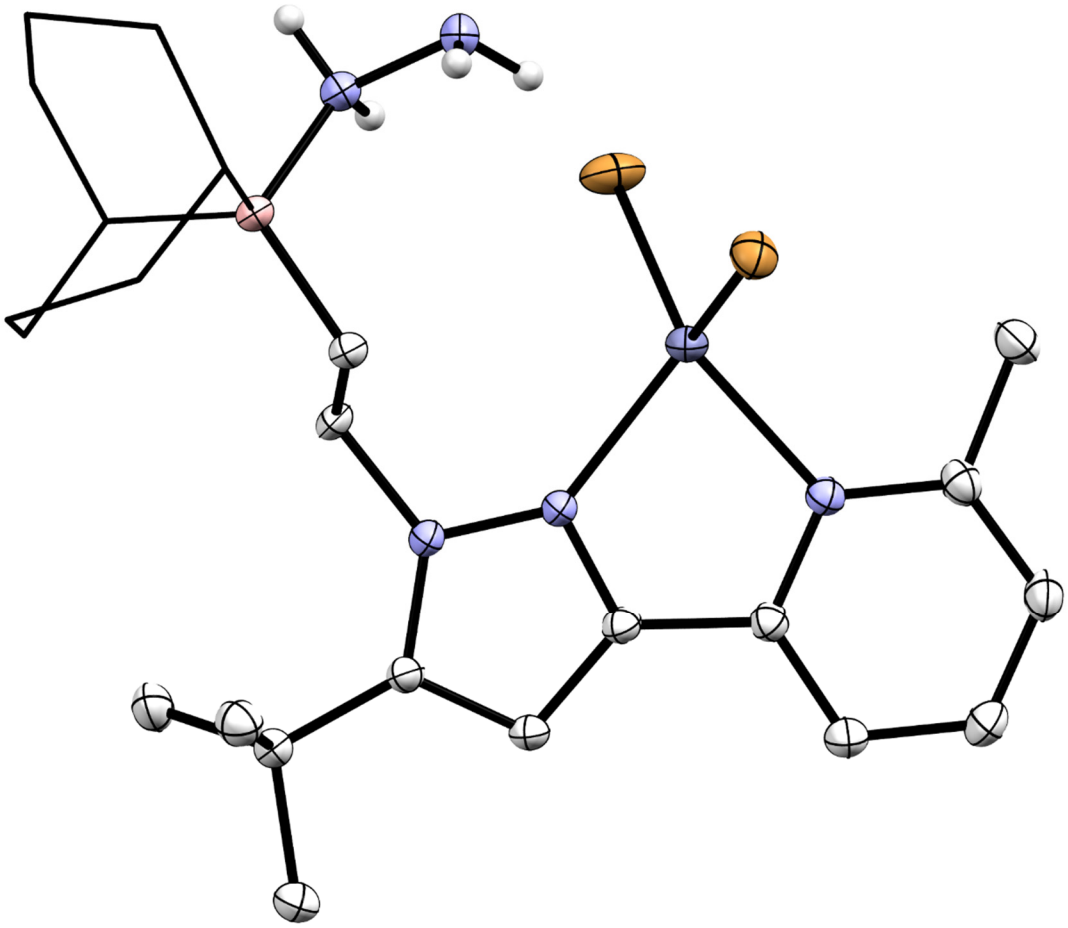


Figure S75 Molecular structure of ($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity.

Complex: $[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr_2]_2(N_2H_4)$

Local name: ML73

CCDC: 2012074

Table S7 Experimental parameters for $[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr_2]_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{46}H_{72}B_2Br_4N_8Zn_2 \cdot 0.206(C_6H_{14}) \cdot 2.044(C_4H_8O)$
M_r	1374.25
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	15.0988 (7), 20.3399 (10), 21.5241 (10)
α, β, γ (°)	87.7923 (19), 84.8814 (18), 71.6768 (19)
V (Å^3)	6249.7 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.37
Crystal size (mm)	0.45 × 0.22 × 0.20
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.482, 0.747
No. of measured, independent and observed [$I > 2s(I)$] reflections	145082, 37943, 24725
R_{int}	0.045
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.169, 1.03
No. of reflections	37943
No. of parameters	1459
No. of restraints	534
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.96, -1.04

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

Refinement details:

A THF molecule was refined as disordered in a general position, another around an inversion center, and a third to be disordered with a hexane molecule. The hexane molecule is in conflict with its symmetry created counterpart (by an inversion center). All THF moieties were restrained to have similar geometries. Bond distances and angles in the hexane moiety were restrained to target values. Atoms of the THF molecule disordered with hexane and the hexane molecule were both restrained to be close to isotropic. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.276(7) to 0.724(7) for the THF of O3 and to 0.589(9) to 0.411(9) for the THF-hexane disorder.

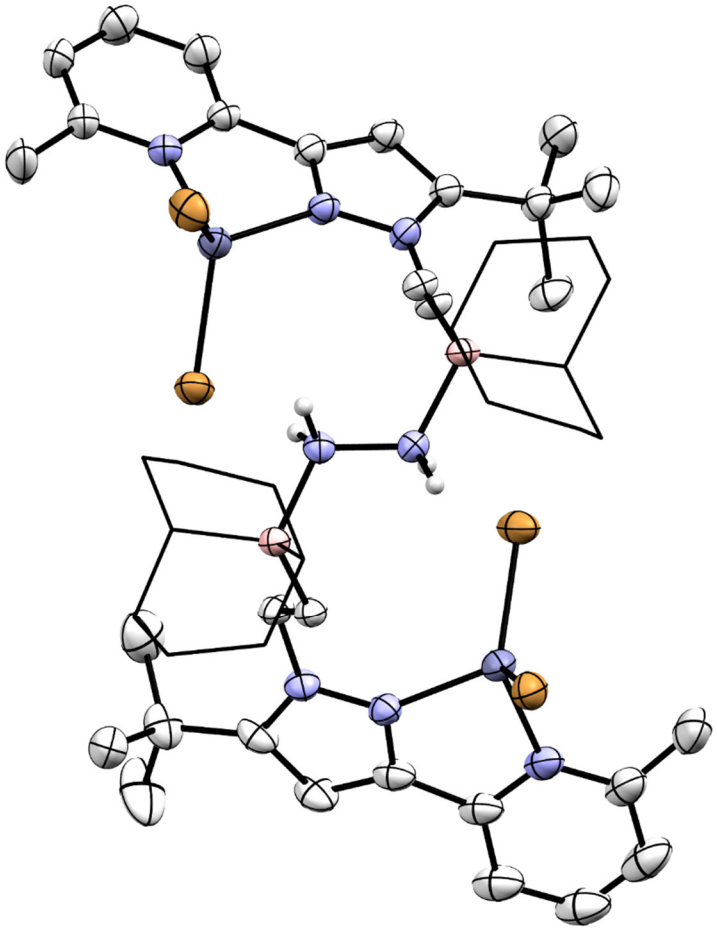


Figure S76 Molecular structure of $[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr_2]_2(N_2H_4)$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituents are displayed in wireframe and solvate molecules are omitted for improved clarity.

Complex: ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$

Local name: EN2155

CCDC: 2012072

Table S8 Experimental parameters for ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)$ZnBr_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{25}H_{42}BBr_2N_5Zn{\cdot}0.5(C_6H_6)$
M_r	687.69
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	12.0353 (8), 24.2453 (15), 21.5350 (12)
β (°)	92.423 (2)
V (Å^3)	6278.3 (7)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	3.35
Crystal size (mm)	0.55 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.371, 0.747
No. of measured, independent and observed [$I > 2s(I)$] reflections	43551, 11598, 8441
R_{int}	0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.06
No. of reflections	11598
No. of parameters	347
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, -0.87

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev1030 (Hübschle *et al.*, 2011).

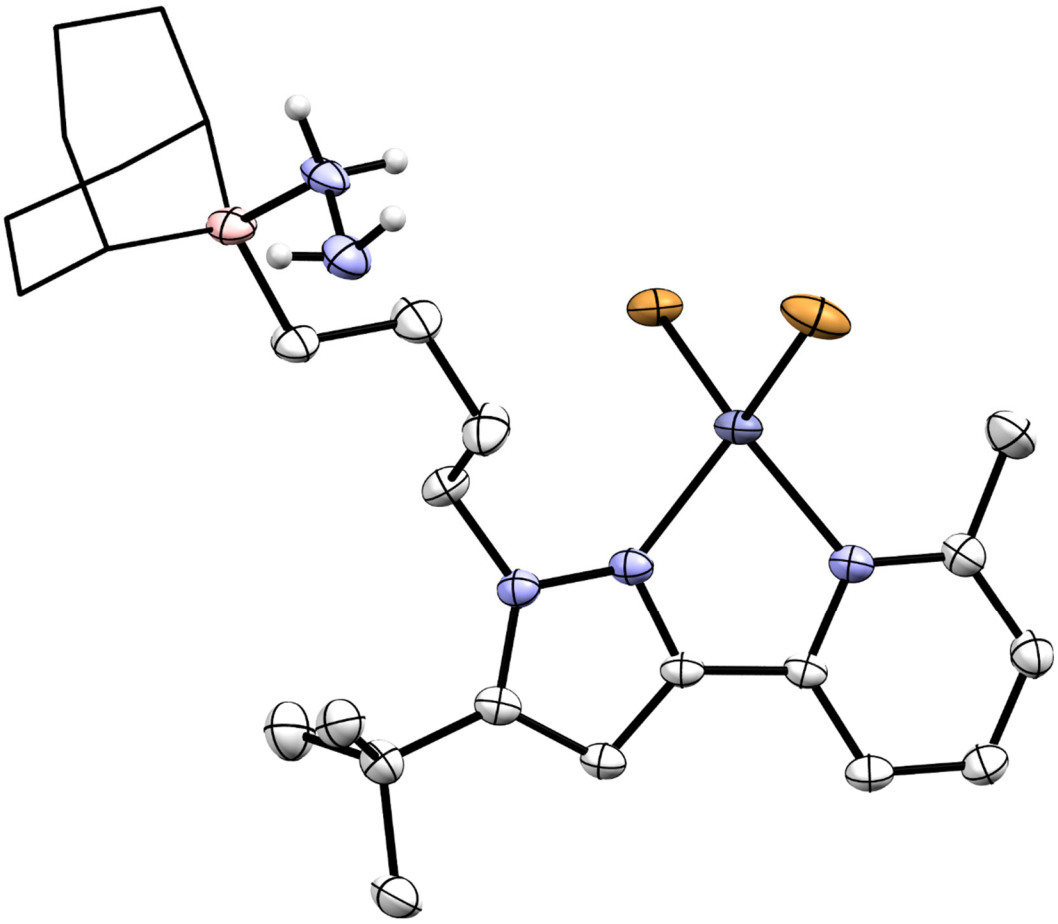


Figure S77 Molecular structure of ($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity.

Complex: [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]

Local name: ML87

CCDC: 2012071

Table S9 Experimental parameters for [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf].

Crystal data	
Chemical formula	$C_{28}H_{46}BBrF_3N_5O_4SZn$
M_r	761.85
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	11.5579 (7), 12.4732 (8), 14.2722 (9)
α, β, γ (°)	106.920 (2), 101.436 (2), 113.029 (2)
V (Å^3)	1693.94 (19)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.02
Crystal size (mm)	0.45 × 0.42 × 0.29
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10.
T_{min}, T_{max}	0.612, 0.747
No. of measured, independent and observed [$I > 2s(I)$] reflections	97174, 13028, 10491
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.773
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.086, 1.05
No. of reflections	13028
No. of parameters	420
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.00, -0.75

Computer programs: Apex3 v2018.7-2 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2018), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev1014 (Hübschle *et al.*, 2011).

Refinement details:

Amine H atom positions were refined and N-H distances were restrained to 0.91(2) Å. H atoms of one methylene group (C15) were substantially deflected from their calculated positions (possibly due to a short contact with H14A in a neighboring molecule) and were instead refined with a C-H distance restraint of 0.99(2) Å.

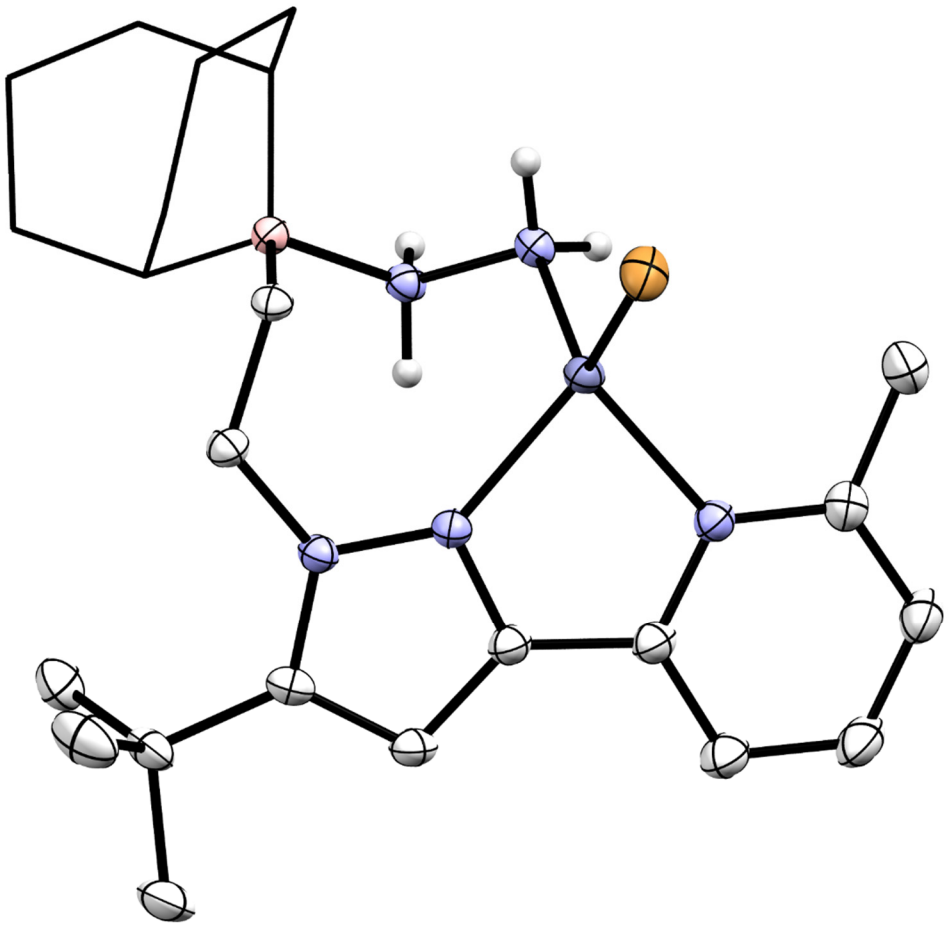


Figure S78 Molecular structure of [($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity. Co-crystallized THF and the counter-anion, trifluoromethanesulfonate, are not displayed but do participate in hydrogen bonding with the hydrazine ligand.

Complex: [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf]

Local name: JK5198

CCDC: 2012073

Table S10 Experimental parameters for [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf].

Crystal data	
Chemical formula	$C_{24}H_{40}BBrN_5Zn{\cdot}CF_3O_3S$
M_r	703.77
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	11.9524 (6), 11.9577 (6), 12.1827 (7)
α, β, γ (°)	107.2938 (19), 93.865 (2), 110.9613 (18)
V (Å^3)	1522.69 (14)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.24
Crystal size (mm)	0.21 × 0.20 × 0.13
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.639, 0.747
No. of measured, independent and observed [$I > 2s(I)$] reflections	89090, 11665, 8964
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.093, 1.03
No. of reflections	11665
No. of parameters	366
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.84, -1.05

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev985 (Hübschle *et al.*, 2011).

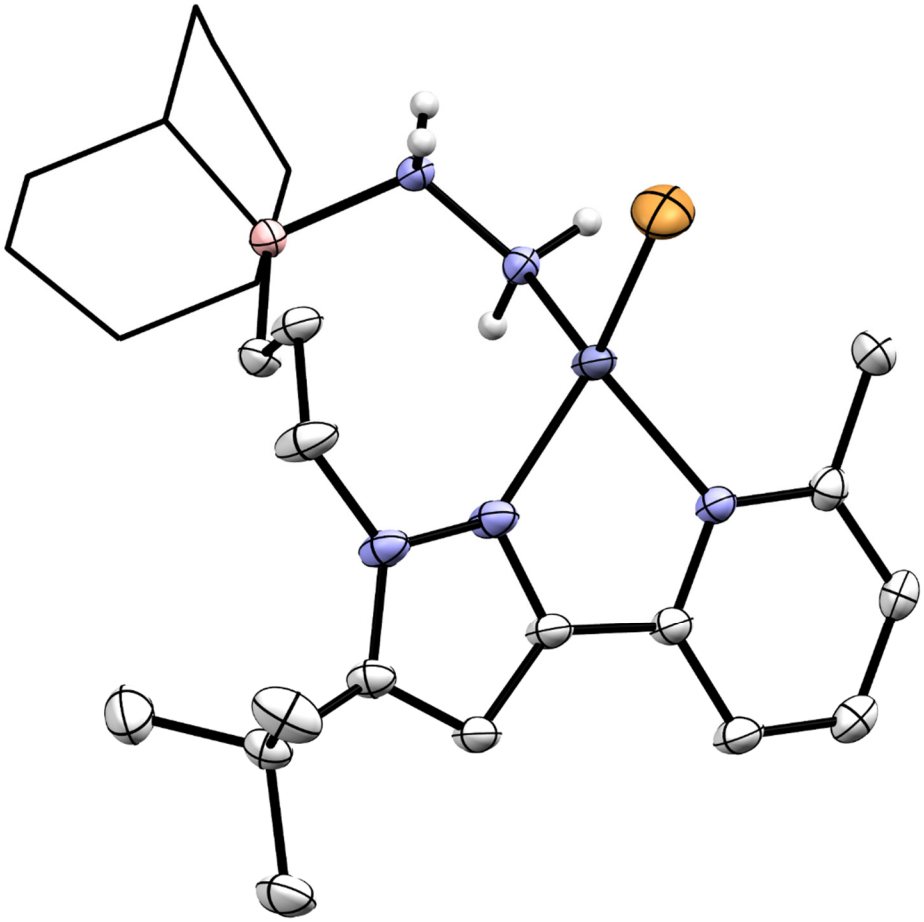


Figure S79 Molecular structure of [($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][OTf] displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity. The counter-anion, trifluoromethanesulfonate, is not displayed but does participate in hydrogen bonding with the hydrazine ligand.

Complex: [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6]

Local name: EN2199

CCDC: 2012075

Table S11 Experimental parameters for [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6].

Crystal data	
Chemical formula	$C_{25}H_{42}BBrN_5Zn{\cdot}F_6P{\cdot}CH_2Cl_2$
M_r	798.62
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	27.6433 (13), 15.2931 (8), 18.2871 (9)
β (°)	119.6838 (15)
V (Å^3)	6716.4 (6)
Z	8
Radiation type	Mo *K*α
μ (mm^{-1})	2.19
Crystal size (mm)	0.33 × 0.21 × 0.19
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.630, 0.747
No. of measured, independent and observed [I > 2s(I)] reflections	84422, 12839, 9789
R_{int}	0.035
(sin θ/λ)$_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.117, 1.04
No. of reflections	12839
No. of parameters	478
No. of restraints	295
H-atom treatment	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	1.39, -1.05

Computer programs: Apex3 v2018.7-2 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2018), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev1030 (Hübschle *et al.*, 2011).

Refinement details:

A methylene chloride molecule was refined as disordered with four alternative orientations. The disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.312(3), 0.319(2), 0.253(2) and 0.115(2).

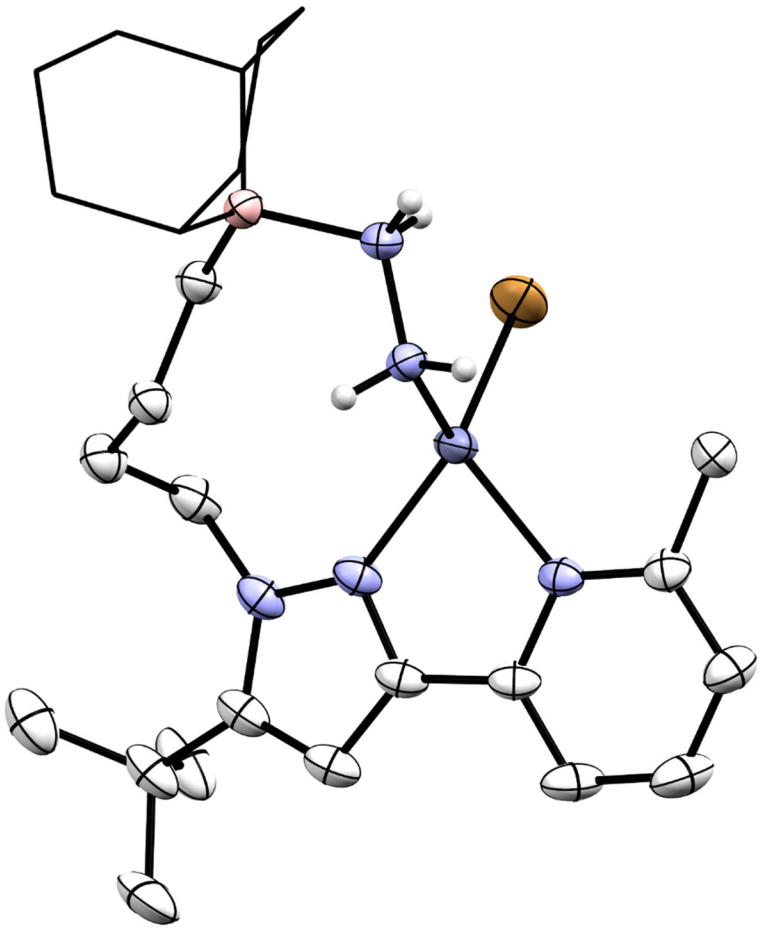


Figure S80 Molecular structure of [($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)][PF_6] displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity. The counter-anion, hexafluorophosphate, is not displayed but does participate in hydrogen bonding with the hydrazine ligand.

Complex: ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3)

Local name: JK5157

CCDC: 2012068

Table S12 Experimental parameters for ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3).

Crystal data	
Chemical formula	$C_{24}H_{39}BBrN_5Zn$
M_r	553.69
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, *b*, *c* (Å)	10.8931 (6), 11.4206 (7), 12.3188 (7)
α, β, γ (°)	83.305 (2), 63.943 (2), 73.559 (2)
V (Å^3)	1320.42 (13)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.46
Crystal size (mm)	0.40 × 0.18 × 0.13
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.543, 0.746
No. of measured, independent and observed [$I > 2s(I)$] reflections	22737, 6327, 5117
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.097, 1.08
No. of reflections	6327
No. of parameters	303
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.15, -0.73

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

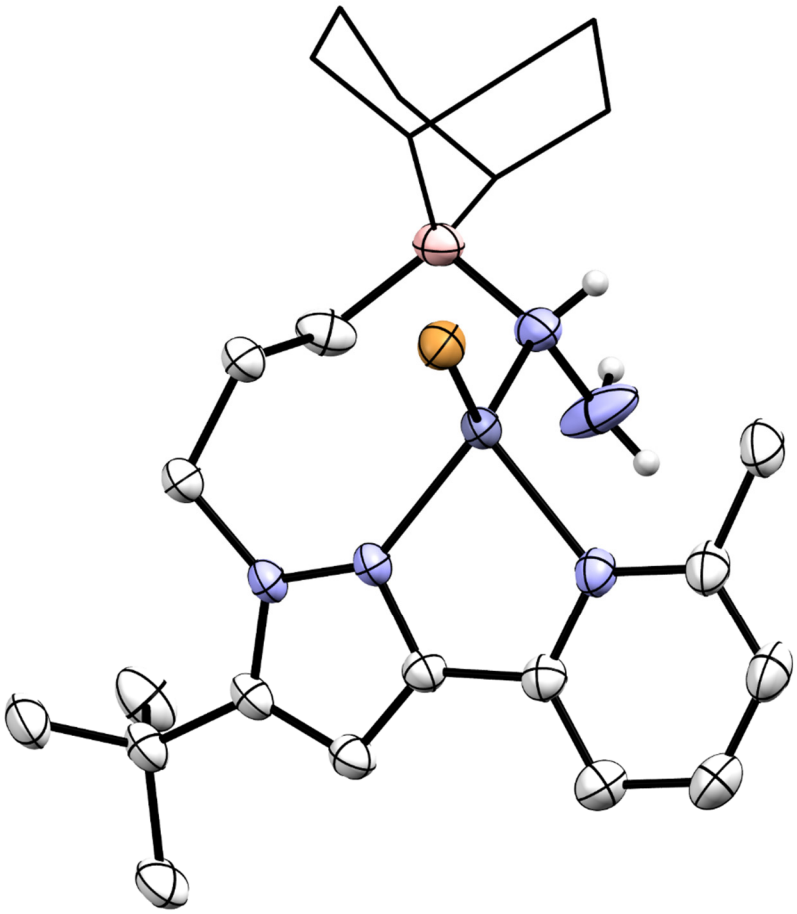


Figure S81 Molecular structure of ($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_3) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN substituent is displayed in wireframe for improved clarity.

Complex: $[Zn(OPEt_3)_4][PF_6]_2$

Local name: JK5220B

CCDC: 2012069

Table S13 Experimental parameters for $[Zn(OPEt_3)_4][PF_6]_2$.

Crystal data	
Chemical formula	$C_{24}H_{60}O_4P_4Zn{\cdot}2(F_6P)$
M_r	891.91
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	150
a, b, c (Å)	12.4190 (12), 12.4357 (12), 30.319 (3)
α, β, γ (°)	89.995 (3), 90.007 (3), 119.911 (3)
V (Å^3)	4058.8 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.93
Crystal size (mm)	0.52 × 0.39 × 0.11
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.561, 0.746
No. of measured, independent and observed [$I > 2s(I)$] reflections	87108, 24707, 20212
R_{int}	0.073
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.186, 1.06
No. of reflections	24707
No. of parameters	1454
No. of restraints	5191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.17, -1.00

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev988 (Hübschle *et al.*, 2011).

Refinement details:

The structure emulates a trigonal setting, approximate $P\bar{3}$ symmetry. Application of this symmetry does introduce substantial additional disorder. The structure was instead refined in a triclinic setting as a 3-component twin, by 120° rotations around the a-axis (twin transformation matrix 0 1 0 / -1 -1 0 / 0 0 1, applied twice). Twin ratios refined to 0.4652(9), 0.2518(9), and 0.283(1). The deviation from the expected values of 0.33 for perfect twinning or actual three-fold symmetry indicates the triclinic symmetry to be correct.

Extensive disorder remains, even in the triclinic setting. For the cation of Zn1, three of the triethyl phosphine oxides moieties were refined as disordered. For the cation of Zn2, two of the triethyl phosphine oxides moieties and the zinc atom were refined as disordered. A common disorder ratio was used for each of the cations. The three PF_6 anions in general positions were each refined as disordered.

All triethyl phosphine oxides moieties were restrained to have similar geometries. All disordered Zn-O bond lengths were restrained to be similar. All P-F distances and all F-P-F close to 90 degree were each restrained to be similar. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.541(5) to 0.459(5) for the phosphine oxide of P1, P2 and P3; to 0.526(4) to 0.474(4) for the phosphine oxide of P6 and P8; to 0.535(6) to 0.465(6) for the PF_6 anions of P11; to 0.745(7) to 0.255(7) for the PF_6 anions of P12; and to 0.646(10) to 0.354(10) for the PF_6 anions of P13.

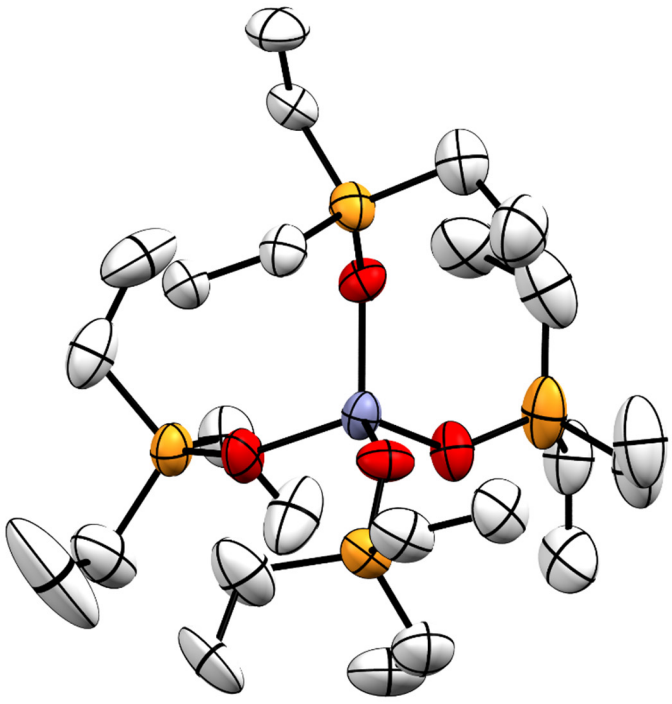


Figure S82 Molecular structure of the cationic portion of $[Zn(OPEt_3)_4][PF_6]_2$ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

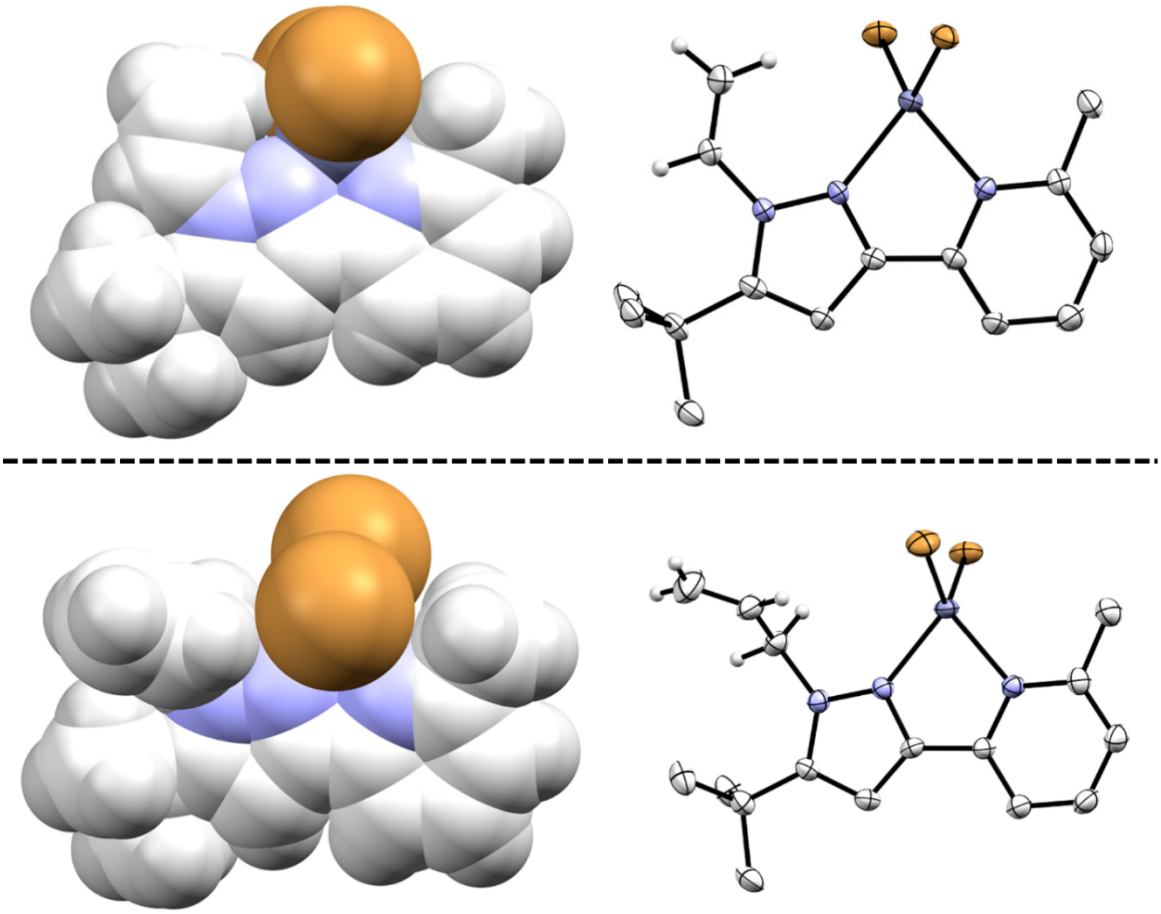


Figure S83 Spacefill model for (^{vinyl}NN^{tBu})ZnBr$_2$ (top) compared to the previously reported compound, (^{allyl}NN^{tBu})ZnBr$_2$ (bottom).

Table S14 Experimentally determined bond distances and angles of cationic hydrazine compounds and hydrazido compound.

Compound	**[($^{2\text{-BBN}}$NN^{tBu})ZnBr(N$_2$H$_4$)]$^+$**	**[($^{3\text{-BBN}}$NN^{tBu})ZnBr(N$_2$H$_4$)]$^+$**	**[($^{4\text{-BBN}}$NN^{tBu})ZnBr(N$_2$H$_4$)]$^+$**	**($^{3\text{-BBN}}$NN^{tBu})ZnBr(N$_2$H$_3$)**
Local name	ML87	JK5198	EN2199	jk5157
Zn-Br1	2.3097(2)	2.3225(3)	2.3177(3)	2.3516(4)
Zn-Br2	n/a	n/a	n/a	n/a
Zn-N$_{hydrazine}$	2.0256(11)	2.0576(13)	2.0892(15)	1.973(2)
Zn-N$_{pyridine}$	2.0726(11)	2.0513(12)	2.0504(14)	2.092(2)
Zn-N$_{pyrazole}$	2.0190(11)	2.0269(13)	2.0299(14)	2.061(2)
B-N	1.6463(18)	1.675(2)	1.668(2)	1.630(4)
N-N	1.4647(15)	1.4666(17)	1.4601(19)	1.476(3)
τ_4	0.84	0.851	0.829	0.857
ΣBα	322.05(10)	319.22(12)	318.69(14)	322.8(2)

Table S15 Experimentally determined bond distances and angles of non-borane containing complexes.

Compound	(^{vinyl}NN^{tBu})ZnBr$_2$	(^{allyl}NN^{tBu})ZnBr$_2$	(^{butenyl}NN^{tBu})ZnBr$_2$	(^{butyl}NN^{tBu})ZnBr$_2$
Local name	ML183		jk2518	jk2517
Previously reported?		yes		
Zn-Br1	2.3516(5)	2.3427(4)	2.3535(5)	2.3473(5)
Zn-Br2	2.3435(6)	2.3466(4)	2.3413(5)	2.3332(5)
Zn-N$_{pyridine}$	2.065(3)	2.0808(19)	2.081(3)	2.070(3)
Zn-N$_{pyrazole}$	2.077(3)	2.0481(19)	2.059(2)	2.057(3)
τ_4	0.8815	0.897	0.85	0.882
notes			2 / unit cell*	

*data for molecule labeled Zn1.

Table S16 Experimentally determined bond distances and angles of three-coordinate borane containing complexes.

Compound	($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$	($^{3\text{-}BBN}$NN^{tBu})ZnBr$_2$	($^{4\text{-}BBN}$NN^{tBu})ZnBr$_2$
Local name	ML141	EEN131	jk2519
Previously reported?		yes	
Zn-Br1	2.3719(5)	2.3500(4)	2.3527(5)
Zn-Br2	2.3393(5)	2.3323(4)	2.3448(5)
Zn-N$_{pyridine}$	2.074(3)	2.0758(19)	2.078(2)
Zn-N$_{pyrazole}$	2.063(3)	2.055(2)	2.060(2)
τ_4	0.878	0.865	0.88
ΣBα	358.4(3)	359.70(3)	359.9(3)
notes	2 / unit cell		

Table S17 Experimentally determined bond distances and angles of borane-hydrazine adducts.

Compound	($^{2\text{-}BBN}$NN^{tBu})ZnBr$_2$(N_2H_4)	($^{3\text{-}BBN}$NN^{tBu})ZnBr$_2$(N_2H_4)	($^{4\text{-}BBN}$NN^{tBu})ZnBr$_2$(N_2H_4)
Local name	ML73_2	JK4287	EN2155
Previously reported?		yes	
Zn-Br1	2.3619(3)	2.3769(6)	2.3572(3)
Zn-Br2	2.3569(3)	2.3420(5)	2.3425(3)
Zn-N$_{hydrazine}$	n/a	n/a	n/a
Zn-N$_{pyridine}$	2.0860(15)	2.074(3)	2.0773(15)
Zn-N$_{pyrazole}$	2.0519(14)	2.042(3)	2.0427(15)
B-N	1.651(3)	1.651(5)	1.649(3)
Zn….NH$_2$(B)	4.352	4.642	4.425*
Zn….NH$_2$(terminal)	4.156	4.252	4.348*
τ_4	0.815	0.901	0.833
ΣBα	321.95(14)	322.0(3)	320.22(16)

*Measured as an intermolecular distance to adjacent molecule. Within the same molecule, the distances are 7.504 and 7.882 Å.

Table S18 Experimentally determined bond distances and angles of borane-hydrazine adducts.

Compound	**$[(^{2\text{-BBN}}NN^{tBu})ZnBr_2]_2(N_2H_4)$**	**$[(^{3\text{-BBN}}NN^{tBu})ZnBr_2]_2(N_2H_4)$**
Local name	ML73	JK4288
Previously reported?		yes
Zn-Br1	2.3609(5)/2.3487(5)	2.3253(9)/2.3101(9)
Zn-Br2	2.3604(6)/2.3696(5)	2.3604(8)/2.3635(8)
$Zn\text{-}N_{hydrazine}$	n/a	n/a
$Zn\text{-}N_{pyridine}$	2.063(3)/2.080(3)	2.083(4)/2.075(4)
$Zn\text{-}N_{pyrazole}$	2.050(3)/2.051(3)	2.069(4)/2.061(4)
B-N	1.697(4)/1.678(4)	1.688(7)/1.676(7)
τ_4	0.863/0.842	0.893/0.884
ΣBα	320.8(2)/322.1(2)	320.3(5)/320.3(4)
notes	2 / unit cell	

Determination of Acceptor Numbers

Acceptor numbers were determined by the Gutmann-Beckett method[7] via the equation:

$$\text{acceptor number} = 2.21 \times (\delta_{sample} - 41.0)$$

where δ_{sample} is the experimentally determined chemical shift in the ^{31}P NMR.

For each determination of a zinc complex, 0.250 mL of a triethylphosphine oxide stock solution (0.1242 M, THF) were combined with an equimolar amount of substrate in 0.500 mL THF and stirred at room temperature for 10 minutes. In a separate vial, an equimolar amount of $TlPF_6$ was dissolved in 0.250 mL THF. The solution containing Zn was transferred to the $TlPF_6$ solution, resulting in an immediate white precipitate. The reaction was stirred 5 minutes, then filtered into a screw cap NMR tube. A sealed triethylphosphine oxide capillary was added and the ^{31}P NMR spectra were referenced to this internal standard (+43.36 ppm). The ^{31}P resonances are reported relative to phosphoric acid. Multiple attempts were made to grow single, X-ray qualtity crystals of these adducts. Unfortunately, all attempts resulted in single crystals of $[Zn(OPEt_3)_4][PF_6]_2$ (see crystallography section above).

For each determination of $PhCH_2CH_2BPin$[8] and $PhCH_2CH_2BBN$,[9] 0.500 mL of a triethylphosphine oxide stock solution (0.1242 M, THF) was combined with an equimolar amount of substrate in 0.500 mL THF. The solutions stirred at room temperature for 20 minutes, then were transferred to a screw-cap NMR tube. A sealed triethylphosphine oxide capillary was added and the ^{31}P NMR spectra were referenced to this internal standard (+43.36 ppm). The ^{31}P resonances are reported relative to phosphoric acid.

Table S19. Acceptor numbers of zinc complexes and model substrates

Compound	^{31}P δ (ppm)	Full Width at Half Max (Hz)	Acceptor Number
No Substrate	43.4	5.6	5.2
$PhCH_2CH_2BPin^a$	43.2 ± 0.04	14.1	4.8 ± 0.1
$PhCH_2CH_2BBN^a$	52.3 ± 0.06	19.2	25.0 ± 0.1
$(^{butyl}NN^{tBu})ZnBr_2{}^b$	71.0 ± 0.1	51	66.3 ± 0.2
$(^{2\text{-}BBN}NN^{tBu})ZnBr_2{}^b$	70.2 ± 0.3	39	64.6 ± 0.7
$(^{3\text{-}BBN}NN^{tBu})ZnBr_2{}^a$	70.6 ± 0.2	60	65.4 ± 0.4
$(^{4\text{-}BBN}NN^{tBu})ZnBr_2{}^a$	70.8 ± 0.01	75	65.8 ± 0.1

[a] average of two trials. [b] average of three trials.

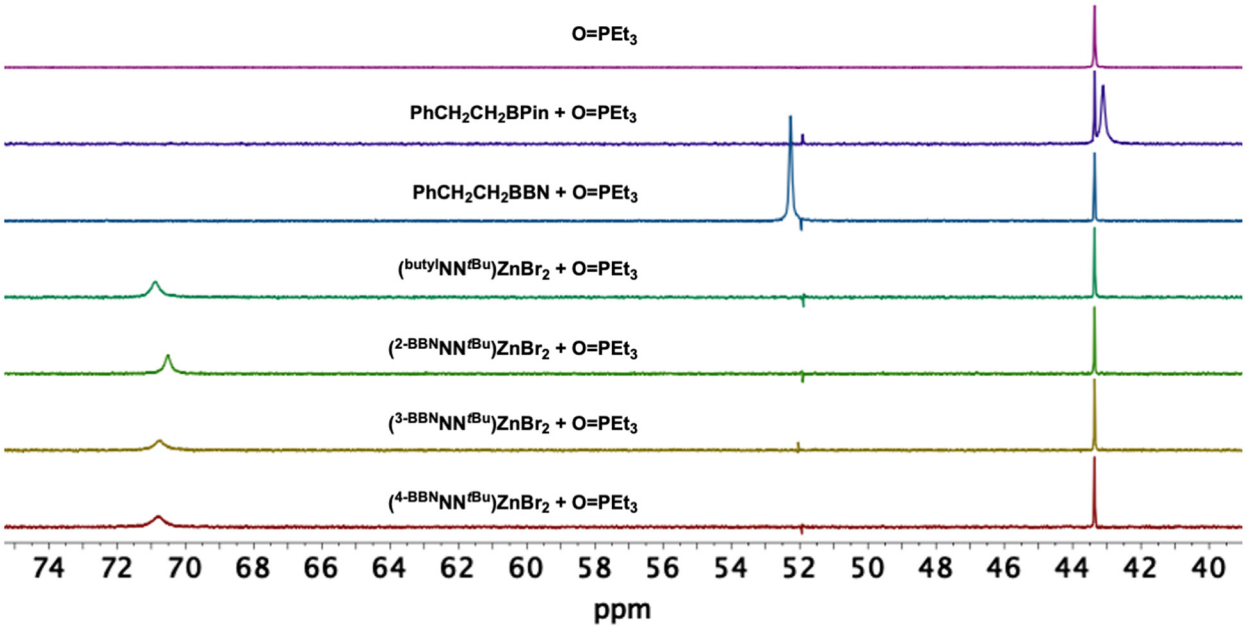
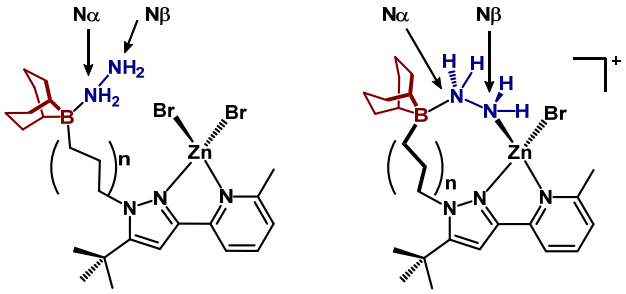


Figure S84. ^{31}P NMR spectra (THF, 25 °C) for determination of acceptor number. The resonance at +43.36 ppm corresponds to an internal (sealed capillary) $OPEt_3$ reference.

Computational Details

DFT calculations were performed using the Gaussian 09 revD01 software package[10] using the B3LYP functional[11] and an ultrafine integration grid for all atoms. Charges and Wiberg bond indices were determined using NBO version 3.1.[12] All reported compounds underwent geometry optimization with the 6-31G(d) basis set,[13] followed by vibrational frequency calculations. These were used to verify that the structures were truly local energetic minima by the absence of imaginary vibrational modes and to provide entropies of formation at 25 °C. Energies were determined by applying the free energy and enthalpy corrections from the frequency calculations to the scf energies from single point calculations of the optimized geometries using the higher-level 6-311+G(2d,p)[14] basis set for all atoms except Zn, which was treated with 6-311+G(2d),[15] with a polarizable continuum model of dichloromethane solvent correction. The single point calculations were used in charge and Wiberg bond index analysis. For determination of Brønsted acidity (see below), an acetonitrile solvation model was used with the same 6-311+G(2d,p) basis set for all atoms except Zn, which was treated with 6-311+G(2d). The calculated pKa values were calibrated to those of pyridine/pyridinium.[16]

Table S20. Wiberg bond index analysis of Zn complexes

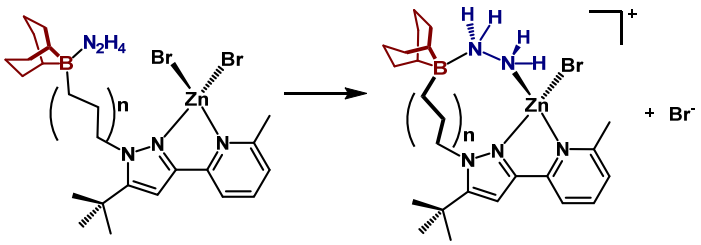


Compound	Zn-N_β	N_α- N_β	N_α-B	N_α-$H_{\alpha1}$	N_α-$H_{\alpha2}$	N_β-$H_{\beta1}$	N_β-$H_{\beta2}$
$[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	0.24	1.01	0.51	0.70	0.69	0.70	0.71
$[(^{3\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	0.24	1.01	0.50	0.69	0.68	0.71	0.70
$[(^{4\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	0.24	1.01	0.50	0.75	0.78	0.81	0.81
$(^{3\text{-BBN}}NN^{t\text{Bu}})ZnBr_2(N_2H_4)$	--	1.01	0.55	0.79	0.77	0.85	0.85

Table S21. Natural charge analysis of Zn complexes

Compound	Zn	B	N_α	N_β	$H_{\alpha1}$	$H_{\alpha2}$	$H_{\beta1}$	$H_{\beta2}$
$[(^{2\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	1.07	0.81	-0.57	-0.68	0.42	0.42	0.42	0.42
$[(^{3\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	1.07	0.83	-0.58	-0.68	0.42	0.43	0.41	0.42
$[(^{4\text{-BBN}}NN^{t\text{Bu}})ZnBr(N_2H_4)]^+$	1.08	0.82	-0.59	-0.68	0.43	0.42	0.42	0.41
$(^{3\text{-BBN}}NN^{t\text{Bu}})ZnBr_2(N_2H_4)$	0.91	0.79	-0.60	-0.64	0.40	0.41	0.37	0.37

Table S22. Thermodynamics of Zn-N_2H_4 bond forming



Compound	ΔG (kcal/mol)
B-2	-159.9
B-3	-158.4
B-4	-161.7

Table S23. Acidification of N_2H_4

Compound	SCF (CH_3CN)	G_{corr}	ΔG	K_{eq}	pK_{eq}	pK_a
Pyridine	-248.363	0.061514				
$[Pyridinium]^+$	-248.809	0.061514				12.33
NH_2NH_2	-111.92	0.030744				
NH_2NH^-	-111.375	0.01306	60.9	1.29E-45	44.9	57.2
MethylBBN-NH_2NH_2	-490.109	0.269219				
MethylBBN-NH_2NH^-	-489.58	0.25365	51.4	1.24E-38	37.9	50.2
MethylBBN-$NHNH_2^-$	-489.608	0.252936	33.6	1.63E-25	24.8	37.1
$[(^{butyl}NN^{tBu})ZnBr(N_2H_4)]^+$	-5289.85	0.39605				
$(^{butyl}NN^{tBu})ZnBr(NH_2NH)$	-5289.33	0.379341	48.9	8.99E-37	36.0	48.4
$(^{butyl}NN^{tBu})ZnBr(NHNH_2)$	-5289.36	0.379755	28.6	7.88E-22	21.1	33.4
$[(^{2\text{-}BBN}NN^{tBu})ZnBr(N_2H_4)]^+$	-5548.84	0.542420				
$(^{2\text{-}BBN}NN^{tBu})ZnBr(NH_2NH)$	-5548.37	0.527752	19.2	7.25E-15	14.1	26.5
$(^{2\text{-}BBN}NN^{tBu})ZnBr(NHNH_2)$	-5548.37	0.528555	18.0	5.54E-14	13.3	25.6
$[(^{3\text{-}BBN}NN^{tBu})ZnBr(N_2H_4)]^+$	-5588.17	0.569517				
$(^{3\text{-}BBN}NN^{tBu})ZnBr(NH_2NH)$	-5587.69	0.553965	19.7	2.97E-15	14.5	26.9
$(^{3\text{-}BBN}NN^{tBu})ZnBr(NHNH_2)$	-5587.7	0.555253	17.0	2.77E-13	12.6	24.9
$[(^{4\text{-}BBN}NN^{tBu})ZnBr(N_2H_4)]^+$	-5627.49	0.597666				
$(^{4\text{-}BBN}NN^{tBu})ZnBr(NH_2NH)$	-5627.01	0.581453	20.6	6.48E-16	15.2	27.5
$(^{4\text{-}BBN}NN^{tBu})ZnBr(NHNH_2)$	-5627.02	0.583888	17.0	3.05E-13	12.5	24.8

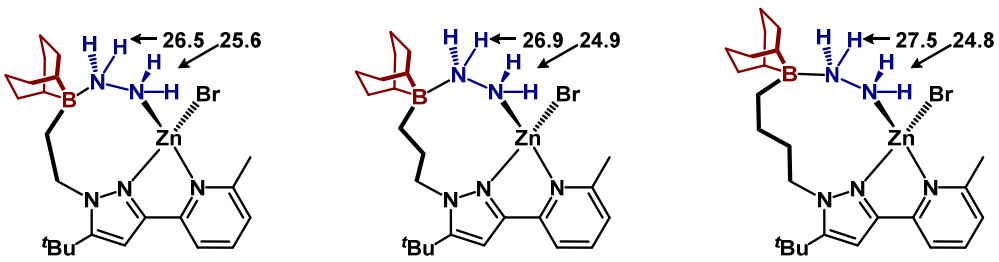


Figure S85. pK_a values for hydrazine protons in **C-2** (left), **C-3** (center), and **C-4** (right)

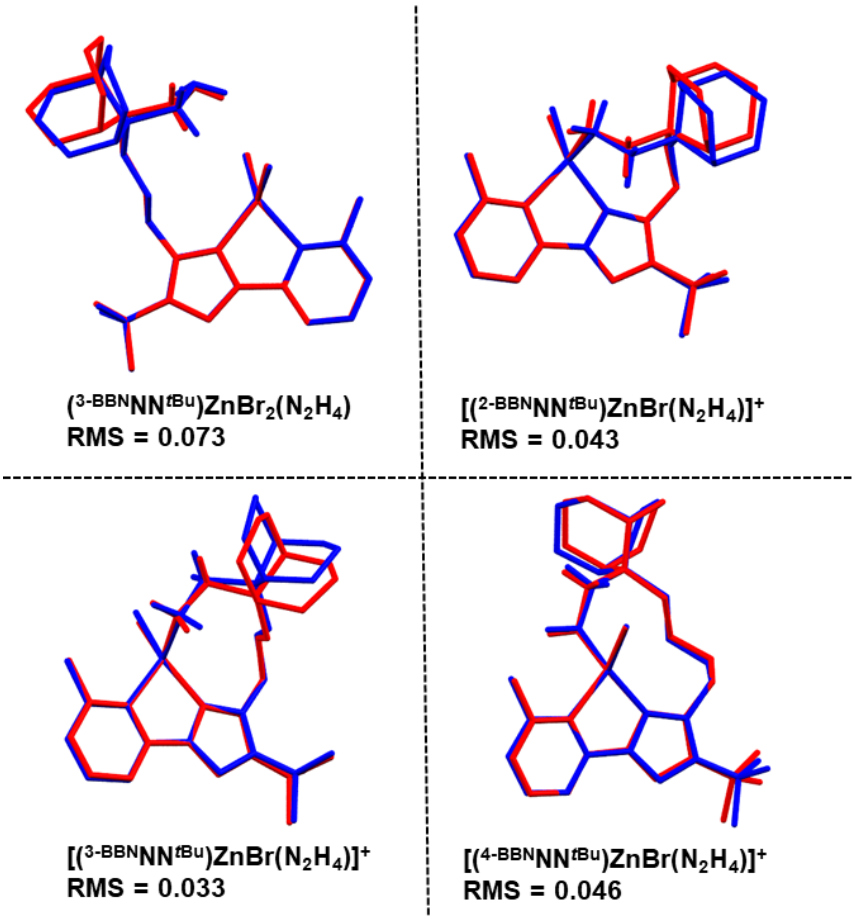


Figure S86. Structural overlays of DFT optimized geometries and molecular structures. Molecular structure is in red, with the DFT optimized geometries in blue. Overlay similarities (RMS) are included. Hydrogen atoms not attached to heteroatoms are omitted for clarity.

Optimized Coordinates

N_2H_4

N	3.41827900	-0.60260000	0.65862700
H	4.06537400	-1.32008700	0.97220600
H	3.11230800	-0.09249500	1.48733000
N	4.13455500	0.23839300	-0.25820200
H	4.59303500	1.01738100	0.21462800
H	3.44974300	0.63680500	-0.89392700

$N_2H_3^-$

N	0.76655600	0.10485000	0.05812500
H	1.12829300	-0.49328200	-0.71696400
N	-0.70398400	-0.06181700	-0.17584000

H	-1.11698500	0.88656800	-0.25463100
H	-1.12755100	-0.37402500	0.71786100

MethylBBN-N_2H_4

B	7.38318800	3.69251400	9.40842400
C	8.30029500	2.58900700	10.19288400
H	7.98537500	2.46224700	11.24357100
C	9.75069800	3.13695000	10.23825600
H	9.75535900	4.02105200	10.88794900
H	10.42180000	2.41034000	10.72080100
C	10.35175400	3.52566000	8.86649000
H	10.73001600	2.62731600	8.36894200
H	11.23834200	4.15197800	9.03248200
C	9.38662300	4.27038500	7.91375500
H	9.82632600	4.27533500	6.90489300
H	9.33365800	5.32301300	8.21972200
C	7.93713200	3.71901100	7.87363200
H	7.36877000	4.41732900	7.23367500
C	7.83227900	2.32111100	7.20934900
H	6.76629900	2.08366200	7.04219500
H	8.26857000	2.33527100	6.19966400
C	8.47358400	1.16095400	8.00554700
H	9.55292200	1.16745300	7.83374800
H	8.12399900	0.20404200	7.59485500
C	8.20652500	1.18976400	9.52861100
H	8.89251700	0.48219700	10.01722500
H	7.20457600	0.76647700	9.72000700
N	5.83065500	3.07908400	9.39449400
H	5.81310800	2.12733000	9.02682400
H	5.49420300	2.99914300	10.35584000
N	4.78766500	3.80411600	8.66487000
H	4.86054400	4.75968200	9.01642900
H	5.14915200	3.86487300	7.71186800
C	7.22589300	5.13418700	10.15120000
H	8.19681500	5.61403300	10.31116800
H	6.63425600	5.87191600	9.58586100
H	6.76705100	5.05659600	11.15021100

MethylBBN-$NHNH_2^-$

B	7.29022300	3.65271100	9.41801000
C	8.29679400	2.59310400	10.20470200
H	7.97412600	2.47370900	11.25369100

C	9.73690700	3.15527000	10.24812400
H	9.72493700	4.05878800	10.87232500
H	10.43030000	2.45447000	10.75050700
C	10.34542800	3.52171900	8.87313400
H	10.72490000	2.61133600	8.39439200
H	11.23682200	4.15116000	9.02798200
C	9.37945600	4.24131400	7.90083200
H	9.84311000	4.23477200	6.89577700
H	9.32328000	5.29887300	8.19236100
C	7.93599900	3.68609300	7.87091800
H	7.36991000	4.36827400	7.20747500
C	7.83063400	2.28267200	7.22887100
H	6.76199600	2.05407400	7.10877300
H	8.25597600	2.26312700	6.20798200
C	8.48145000	1.13601900	8.03925200
H	9.56249900	1.13868000	7.85830000
H	8.13109600	0.16896100	7.64327900
C	8.22282100	1.18534000	9.56496800
H	8.92291300	0.48070800	10.05229000
H	7.22136200	0.77651500	9.76295900
N	5.82546200	3.10173100	9.48005200
N	4.82600000	3.82867300	8.70415300
H	4.53801400	4.60447000	9.30072400
H	5.29721600	4.29378100	7.91796600
C	7.26467200	5.14897100	10.12214000
H	8.23623900	5.66098000	10.17730800
H	6.59393100	5.84520800	9.59037600
H	6.88389000	5.08691100	11.15437600
H	5.75187900	2.14777900	9.13574800

MethylBBN-NH_2NH^-

B	7.34278100	3.66830900	9.39298900
C	8.29831800	2.57399200	10.18583000
H	7.96950800	2.42244800	11.23258000
C	9.73670900	3.14110500	10.26409600
H	9.70966700	4.04155400	10.89418900
H	10.41836600	2.43606900	10.77600200
C	10.36477100	3.51503000	8.90085100
H	10.72621800	2.60249300	8.41169800
H	11.26815600	4.12244600	9.07597300
C	9.41750300	4.27138100	7.93760400
H	9.88370300	4.27902900	6.93477500
H	9.37719900	5.32430500	8.25392400

C	7.96821400	3.73532900	7.88115900
H	7.38186300	4.43308000	7.26406100
C	7.82716200	2.35356000	7.20316500
H	6.74423400	2.19746800	7.08609100
H	8.24988800	2.35869500	6.18105300
C	8.46810800	1.17280700	7.97124500
H	9.54722400	1.15617300	7.77337600
H	8.09030000	0.22166400	7.56121600
C	8.24155800	1.18116600	9.50506700
H	8.96253200	0.48247200	9.96840100
H	7.25417900	0.73538100	9.71038100
N	5.81696200	3.09185600	9.32635400
H	5.85787600	2.08466700	9.17277500
H	5.44838300	3.17279100	10.29531800
N	4.84594100	3.56268300	8.31644900
C	7.21086000	5.11521300	10.15704300
H	8.15053400	5.68326600	10.21503800
H	6.48379000	5.77029800	9.65180700
H	6.85804700	5.00505800	11.19889800
H	5.13205100	4.54994900	8.22041800

[(^{Butyl}NN^{tBu})ZnBr(N_2H_4)]$^+$

Br	4.68476700	4.94739400	4.89158800
Zn	6.23634800	3.98429200	3.45322300
N	7.89094500	4.99188200	2.75382000
N	7.60318400	2.56764200	3.89476500
N	7.68795400	1.30197500	4.36085500
N	3.72436100	2.86625200	2.24781000
H	2.94694700	3.21689700	1.68414400
H	3.56405400	3.18079400	3.21439800
N	4.96318600	3.49488500	1.81383500
H	4.74028100	4.37017700	1.33527700
H	5.35458200	2.85911100	1.11292200
C	6.67349500	7.01386200	2.10560200
C	7.96067800	6.25425500	2.27456200
C	9.19550800	6.81685200	1.93736100
C	10.36021100	6.06990800	2.09502700
C	10.27950500	4.77265700	2.59583600
C	9.02569200	4.26059300	2.92259000
C	8.83618200	2.92076300	3.48902800
C	9.72562500	1.86654600	3.70965100
C	8.97355700	0.83514000	4.27376700
C	9.47075900	-0.54239600	4.70745000
C	10.99807700	-0.60476500	4.47830900

C	9.21535100	-0.78417900	6.21598500
C	8.82378300	-1.65729500	3.84762400
C	6.50650700	0.68176300	5.00164200
H	6.86423600	8.07478900	1.92879700
H	6.11206300	6.63769900	1.23927300
H	6.03668700	6.91802000	2.99169500
H	9.23278800	7.83163800	1.55708300
H	11.32447300	6.49682300	1.83682300
H	11.16988500	4.17254000	2.74355400
H	10.77950600	1.83812800	3.48619100
H	11.36776100	-1.58684300	4.78779900
H	11.25803600	-0.47325800	3.42240200
H	11.52902200	0.14997900	5.06845200
H	9.24596300	-2.62571800	4.13568700
H	7.73914200	-1.72671300	3.96918900
H	9.03240000	-1.50133700	2.78384100
H	9.67298600	0.00428400	6.82329200
H	8.15453900	-0.83780200	6.47240300
H	9.66832900	-1.73719300	6.50833500
C	5.43358148	0.39749301	3.93411149
C	4.12833007	-0.04274891	4.62266491
C	3.97008267	-1.56925002	4.49478945
H	6.79542493	-0.23581567	5.47012447
H	6.10904314	1.34852782	5.73808423
H	5.77440143	-0.38141443	3.28446160
H	5.25418277	1.28477054	3.36362513
H	4.16253824	0.22683006	5.65758373
H	3.29717755	0.44241065	4.15500510
H	4.84507187	-1.98144551	4.03719929
H	3.84078207	-1.99710576	5.46696270
H	3.11444295	-1.78981967	3.89135785

(^{Butyl}NN^{tBu})ZnBr(NH$_2$NH)

Br	4.68476700	4.94739400	4.89158800
Zn	6.23634800	3.98429200	3.45322300
N	7.89094500	4.99188200	2.75382000
N	7.60318400	2.56764200	3.89476500
N	7.68795400	1.30197500	4.36085500
N	3.72436100	2.86625200	2.24781000
N	4.96318600	3.49488500	1.81383500
C	6.67349500	7.01386200	2.10560200
C	7.96067800	6.25425500	2.27456200
C	9.19550800	6.81685200	1.93736100
C	10.36021100	6.06990800	2.09502700

C	10.27950500	4.77265700	2.59583600
C	9.02569200	4.26059300	2.92259000
C	8.83618200	2.92076300	3.48902800
C	9.72562500	1.86654600	3.70965100
C	8.97355700	0.83514000	4.27376700
C	9.47075900	-0.54239600	4.70745000
C	10.99807700	-0.60476500	4.47830900
C	9.21535100	-0.78417900	6.21598500
C	8.82378300	-1.65729500	3.84762400
C	6.50650700	0.68176300	5.00164200
H	6.86423600	8.07478900	1.92879700
H	6.11206300	6.63769900	1.23927300
H	6.03668700	6.91802000	2.99169500
H	9.23278800	7.83163800	1.55708300
H	11.32447300	6.49682300	1.83682300
H	11.16988500	4.17254000	2.74355400
H	10.77950600	1.83812800	3.48619100
H	11.36776100	-1.58684300	4.78779900
H	11.25803600	-0.47325800	3.42240200
H	11.52902200	0.14997900	5.06845200
H	9.24596300	-2.62571800	4.13568700
H	7.73914200	-1.72671300	3.96918900
H	9.03240000	-1.50133700	2.78384100
H	9.67298600	0.00428400	6.82329200
H	8.15453900	-0.83780200	6.47240300
H	9.66832900	-1.73719300	6.50833500
C	5.43358148	0.39749301	3.93411149
C	4.12833007	-0.04274891	4.62266491
C	3.97008267	-1.56925002	4.49478945
H	6.79542493	-0.23581567	5.47012447
H	6.10904314	1.34852782	5.73808423
H	5.77440143	-0.38141443	3.28446160
H	5.25418277	1.28477054	3.36362513
H	4.16253824	0.22683006	5.65758373
H	3.29717755	0.44241065	4.15500510
H	4.84507187	-1.98144551	4.03719929
H	3.84078207	-1.99710576	5.46696270
H	3.11444295	-1.78981967	3.89135785
H	5.44865651	2.85804526	1.21487463
H	4.73663965	4.33793512	1.32604073
H	3.93547211	2.06185296	2.80312458

(^{Butyl}NN^{tBu})ZnBr(NHNH$_2$)

Br	4.68476700	4.94739400	4.89158800

Zn	6.23634800	3.98429200	3.45322300
N	7.89094500	4.99188200	2.75382000
N	7.60318400	2.56764200	3.89476500
N	7.68795400	1.30197500	4.36085500
N	3.72436100	2.86625200	2.24781000
H	2.94694700	3.21689700	1.68414400
H	3.56405400	3.18079400	3.21439800
N	4.96318600	3.49488500	1.81383500
C	6.67349500	7.01386200	2.10560200
C	7.96067800	6.25425500	2.27456200
C	9.19550800	6.81685200	1.93736100
C	10.36021100	6.06990800	2.09502700
C	10.27950500	4.77265700	2.59583600
C	9.02569200	4.26059300	2.92259000
C	8.83618200	2.92076300	3.48902800
C	9.72562500	1.86654600	3.70965100
C	8.97355700	0.83514000	4.27376700
C	9.47075900	-0.54239600	4.70745000
C	10.99807700	-0.60476500	4.47830900
C	9.21535100	-0.78417900	6.21598500
C	8.82378300	-1.65729500	3.84762400
C	6.50650700	0.68176300	5.00164200
H	6.86423600	8.07478900	1.92879700
H	6.11206300	6.63769900	1.23927300
H	6.03668700	6.91802000	2.99169500
H	9.23278800	7.83163800	1.55708300
H	11.32447300	6.49682300	1.83682300
H	11.16988500	4.17254000	2.74355400
H	10.77950600	1.83812800	3.48619100
H	11.36776100	-1.58684300	4.78779900
H	11.25803600	-0.47325800	3.42240200
H	11.52902200	0.14997900	5.06845200
H	9.24596300	-2.62571800	4.13568700
H	7.73914200	-1.72671300	3.96918900
H	9.03240000	-1.50133700	2.78384100
H	9.67298600	0.00428400	6.82329200
H	8.15453900	-0.83780200	6.47240300
H	9.66832900	-1.73719300	6.50833500
C	5.43358148	0.39749301	3.93411149
C	4.12833007	-0.04274891	4.62266491
C	3.97008267	-1.56925002	4.49478945
H	6.79542493	-0.23581567	5.47012447
H	6.10904314	1.34852782	5.73808423
H	5.77440143	-0.38141443	3.28446160

H	5.25418277	1.28477054	3.36362513
H	4.16253824	0.22683006	5.65758373
H	3.29717755	0.44241065	4.15500510
H	4.84507187	-1.98144551	4.03719929
H	3.84078207	-1.99710576	5.46696270
H	3.11444295	-1.78981967	3.89135785
H	5.19110301	3.67640090	0.85722337

($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$)

Br	-0.90131000	8.18735800	3.13964100
Br	1.70152400	10.34380900	0.88721200
Zn	0.30501600	8.45013400	1.11643900
N	-0.57279200	8.16316200	-0.76508700
N	1.11995300	6.63874300	0.61224200
N	1.89431100	5.69559500	1.16963200
N	2.31357400	8.45603900	4.78553500
H	1.40062600	8.20458900	4.38103400
H	2.13874900	8.54757600	5.78672800
N	2.62450800	9.81058900	4.32788300
H	2.10789700	9.96941300	3.46016800
H	3.60618300	9.78231500	4.05782200
C	-1.94126600	10.16284400	-0.57604400
C	-1.43717100	8.99562900	-1.37676100
C	-1.82418900	8.76815200	-2.70212300
C	-1.30172400	7.67614200	-3.39103200
C	-0.40718900	6.82337200	-2.74989700
C	-0.06244400	7.09452100	-1.42536200
C	0.84510600	6.25189600	-0.64009800
C	1.48080400	5.03022600	-0.89993100
C	2.14639500	4.68519000	0.27755500
C	2.96385600	3.42643900	0.54856200
C	4.37912900	3.77167800	1.06730500
C	3.12567100	2.64905200	-0.77658900
C	2.22724000	2.50162800	1.54963200
C	2.22076700	5.86970800	2.61101800
C	3.32116900	6.88836700	2.92303700
C	3.13050100	6.04597200	5.59611400
C	4.18938100	4.92812700	5.39887300
C	5.66003200	5.38302100	5.52006200
C	5.97762000	6.71725600	4.80914700
C	4.91589300	7.83434100	4.98591600
C	4.85910700	8.39302300	6.43285600
C	4.31714200	7.41176700	7.49911500
C	3.09596600	6.56871700	7.05815900

B	3.45373600	7.25283700	4.53209600
H	-1.10610600	10.82029300	-0.30527000
H	-2.67912900	10.74143900	-1.13747100
H	-2.40005800	9.82072800	0.35891800
H	-2.52430900	9.44579300	-3.17860000
H	-1.58960700	7.48997000	-4.42173600
H	0.01760800	5.96602300	-3.26000900
H	3.72846200	1.75226200	-0.59972800
H	2.15968400	2.32382100	-1.17821400
H	3.63440400	3.25080200	-1.53766000
H	4.96223700	2.85023100	1.17668400
H	4.90590200	4.42442400	0.36261300
H	4.36465800	4.26878100	2.03957100
H	2.10592200	2.95535200	2.53694100
H	1.23174100	2.23778000	1.17614500
H	2.79783200	1.57516300	1.68134800
H	1.45649800	4.45730000	-1.81288100
H	1.26787900	6.15057200	3.06925700
H	2.47924200	4.88461800	2.99219600
H	4.27108500	6.50548100	2.52996300
H	3.12678900	7.80789000	2.35073500
H	5.26481900	8.66356200	4.34353800
H	2.14799600	5.57373700	5.42024000
H	5.85585700	8.73467900	6.75200600
H	4.23489000	9.29974600	6.43233700
H	5.12218000	6.73833200	7.80782600
H	4.05387300	7.97559100	8.40507100
H	2.18032700	7.16719800	7.20085300
H	2.97866700	5.72861700	7.76006700
H	4.01439200	4.10497200	6.10953200
H	4.04902500	4.48709100	4.40072600
H	5.92919200	5.45820500	6.57804400
H	6.31236000	4.59652300	5.11431000
H	6.96295900	7.07099400	5.15028800
H	6.09274600	6.52183500	3.73386300

($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$)

C	6.26249500	-1.28349900	8.11970900
C	6.44659800	-0.22742600	7.06703300
C	5.43999100	0.10839100	6.15406500
C	5.67449200	1.10444500	5.20969000
C	6.90909500	1.74807900	5.18305000
C	7.87626400	1.36862000	6.11387100
C	9.21859600	1.95806100	6.16444400
C	9.87499900	2.90676000	5.36669200

C	11.16683400	3.01549400	5.88167400
C	12.30720900	3.89302500	5.37764300
C	11.77450700	4.78534100	4.23499200
C	13.45339200	3.02484300	4.80145400
C	12.83460000	4.82482800	6.49532200
C	12.31557300	1.77739000	7.86882800
C	12.08632200	2.27411600	9.30109500
C	13.13759300	1.71893400	10.27827900
C	12.62965100	3.57232400	12.28536300
C	12.21790500	3.71632300	13.77541100
C	13.12116300	2.97949700	14.79404400
C	13.59489300	1.57397000	14.35400000
C	14.03638300	1.45853800	12.87262800
C	15.34235900	2.23827600	12.56658300
C	15.21824900	3.78076600	12.59237600
C	13.93113800	4.34458200	11.94608600
B	12.86612100	2.00456400	11.87462900
N	7.63646600	0.40292600	7.03365400
N	10.05251000	1.52032900	7.11581200
N	11.22692300	2.14866700	6.94182800
N	11.44156000	1.20489400	12.23360400
H	11.19948800	1.41856800	13.20083100
H	10.67281000	1.57412700	11.65762600
N	11.46449000	-0.24380000	12.14583400
H	12.11722000	-0.47106200	11.39831500
H	10.54150700	-0.53486000	11.81775500
Zn	9.22175600	0.12496700	8.38715000
Br	8.43757900	0.98272800	10.47480800
Br	10.41417700	-1.89009000	8.33012300
H	7.04862100	-2.04369400	8.04272400
H	6.34096500	-0.83816800	9.11876300
H	5.28910000	-1.77157700	8.02654900
H	4.48832900	-0.41047500	6.19324800
H	4.90129300	1.37731700	4.49727900
H	7.12265100	2.52631600	4.45885400
H	9.47665900	3.44274900	4.52030500
H	13.60382300	5.48852000	6.08468800
H	12.02839500	5.44889500	6.89603100
H	13.28305900	4.28053900	7.33009400
H	13.92100800	2.38245300	5.55263300
H	13.08653400	2.38244900	3.99357600
H	14.23485900	3.67442200	4.39111700
H	12.58113700	5.43033100	3.87153800
H	11.41897200	4.18945800	3.38729700
H	10.95698400	5.43068200	4.57449600
H	13.24867600	2.16077100	7.46041500
H	12.36548800	0.68372500	7.85156800
H	12.08853700	3.37159300	9.31376400

H	11.07434300	1.97169500	9.59633900
H	13.24964400	0.63689700	10.08583300
H	14.11566000	2.13795700	10.00448900
H	11.82568200	4.04899600	11.69687400
H	14.26419100	0.39403200	12.69885300
H	14.40881800	1.25802000	15.02520900
H	12.78790900	0.84508600	14.53043800
H	13.99669400	3.60028500	15.00728800
H	12.58820900	2.89845900	15.75238500
H	12.16560400	4.77947200	14.05832400
H	11.18190000	3.35407800	13.89273000
H	14.05487500	4.33960200	10.85315800
H	13.83405800	5.40537400	12.22788500
H	15.28240900	4.13278500	13.62714200
H	16.09170600	4.21867900	12.08793500
H	16.14018600	1.94179700	13.26603600
H	15.69637600	1.93192700	11.57233500

($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr$_2$(N$_2$H$_4$)

Br	4.14588300	2.57190200	14.27434400
Br	1.95148200	-0.88526600	15.01241900
Zn	3.16953300	0.54783600	13.59497900
N	4.42494400	-0.64587700	12.38376500
N	2.30421400	0.82777400	11.72389300
N	1.33657200	1.57618200	11.17100000
N	-3.66127300	3.39857200	15.51785700
H	-2.83767900	2.96458700	15.93881700
H	-4.07914000	4.01003000	16.22257900
N	-4.55116600	2.32774200	15.13205900
H	-5.19675200	2.14117200	15.89801500
H	-5.09246200	2.68786700	14.34856700
C	5.80278400	-1.27747600	14.28037400
C	5.46968700	-1.37473200	12.81885100
C	6.19462600	-2.17755300	11.92983700
C	5.82583100	-2.21981400	10.58770100
C	4.74357700	-1.46116000	10.14900600
C	4.06101400	-0.67802200	11.08066300
C	2.91772300	0.17269100	10.73231000
C	2.31530800	0.50230200	9.50783300
C	1.30098200	1.40917900	9.80907600
C	0.36111300	2.11931000	8.84045800
C	-1.12382200	1.86371400	9.19299000
C	0.65929600	3.63919300	8.80983700
C	0.60728700	1.56381600	7.42036200
C	0.51957300	2.38733200	12.08990300
C	-0.48261000	1.54918400	12.89387600
C	-1.30469300	2.40871900	13.87247900
C	-2.35389300	3.33824700	13.22958300

C	-4.44014600	5.11736000	13.61473500
C	-3.94127700	6.03746500	12.46846000
C	-2.83026700	7.04065800	12.85880500
C	-1.72707900	6.47086200	13.78163300
C	-2.22917400	5.54766400	14.92323200
C	-3.02143400	6.32392200	16.00990200
C	-4.40733800	6.85366900	15.57166800
C	-5.23747400	5.87652500	14.70689400
B	-3.13113100	4.36451000	14.24046800
H	6.01325700	-0.23659900	14.55372300
H	4.94606200	-1.60081900	14.88389500
H	6.67055700	-1.89223000	14.53306900
H	7.03508900	-2.75717500	12.29636200
H	6.37766200	-2.83974100	9.88678400
H	4.43078500	-1.47430900	9.11075400
H	2.58531200	0.14666000	8.52652000
H	1.63349500	1.74890500	7.08493800
H	0.41358400	0.48673200	7.36958000
H	-0.06688600	2.05956900	6.71412600
H	1.70257100	3.82527300	8.53289500
H	0.01717000	4.12528100	8.06633300
H	0.47727400	4.12786900	9.77104600
H	-1.41579200	2.29243400	10.15463300
H	-1.76289200	2.31564800	8.42577800
H	-1.33921800	0.78983500	9.22211600
H	1.22549000	2.88984400	12.75988600
H	0.02044800	3.15241000	11.49933800
H	-1.15627700	1.02252800	12.20479000
H	0.06983000	0.78482700	13.45205400
H	-1.80962500	1.70392100	14.54860600
H	-0.60689900	2.98824000	14.49584600
H	-1.86852600	3.94406200	12.45093600
H	-3.07546200	2.70569400	12.68502100
H	-5.15198000	4.41812200	13.13594100
H	-1.32445300	5.15613200	15.41920600
H	-3.56591500	5.39146600	11.66310600
H	-4.78252900	6.59860000	12.03198600
H	-2.36330500	7.42632500	11.94161200
H	-3.28400000	7.91630700	13.33434900
H	-1.01695800	5.89741400	13.17089200
H	-1.14804800	7.31071700	14.19562800
H	-6.07745600	6.43129000	14.26127900
H	-5.71945300	5.13511400	15.37027700
H	-4.98803400	7.13020400	16.46319000
H	-4.27228900	7.78742400	15.01877200
H	-3.15242000	5.67408200	16.89426200
H	-2.42751200	7.16999400	16.38749200

[($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)]$^+$

C	3.19428900	-0.35826800	6.54089700
C	4.52948500	-1.03742900	6.66676600
C	4.88481400	-1.76194400	7.80977900
C	6.13592700	-2.36830200	7.88221200
C	7.01904700	-2.24790700	6.81108000
C	6.61492100	-1.52065800	5.69387500
C	7.45493000	-1.36035200	4.50080500
C	8.73188300	-1.82844500	4.18527600
C	9.00151300	-1.38564600	2.88805200
C	10.25999900	-1.65772400	2.06499200
C	11.19177700	-2.57672500	2.88749700
C	9.91739000	-2.39649400	0.74749400
C	11.03186700	-0.34709600	1.77480700
C	7.57596000	-0.10998800	1.15283000
C	6.61492700	1.08740400	1.12590400
C	8.55658000	3.03093400	1.66592100
C	8.84517400	3.23538800	0.15232800
C	7.87949400	4.19680300	-0.57703200
C	6.38603000	4.02349500	-0.21461100
C	6.08734200	3.78173800	1.29267100
C	6.33589800	5.04609100	2.15923700
C	7.81688700	5.47102400	2.29245600
C	8.81765900	4.31065300	2.50810300
B	7.01543900	2.53310800	1.78635200
N	5.39291800	-0.92673600	5.63229000
N	6.96027100	-0.65891500	3.46203600
N	7.90384100	-0.66626500	2.49164800
N	6.71800400	2.37965900	3.47165100
H	7.32750300	1.66259300	3.87032900
H	6.94668000	3.27911000	3.90022700
N	5.35075900	2.00583800	3.78406500
H	4.77496000	2.39657700	3.03120000
H	5.05746400	2.46277500	4.64999900
Zn	5.03149500	-0.09585500	3.77034300
Br	3.10303500	-0.59119300	2.63232400
H	5.00033100	3.57465400	1.33830700
H	9.27851000	2.27530700	2.02144800
H	5.76012900	5.89536900	1.76693900
H	5.91429200	4.88610500	3.17094700
H	8.10421100	6.02694300	1.39711000
H	7.91427100	6.18888900	3.11743200
H	5.83231400	4.90480600	-0.56726200
H	5.97762100	3.17824400	-0.78377400
H	8.18572500	5.22922600	-0.38581200
H	7.99671000	4.06149600	-1.65973400
H	9.87502500	3.59300800	0.00971200

H	8.80230500	2.25432000	-0.34331300
H	8.82686000	4.03818200	3.58016200
H	9.83394200	4.68557300	2.32300600
H	3.31002200	0.73365100	6.54521100
H	2.69957900	-0.63513200	5.60331600
H	2.53913700	-0.62206900	7.37399800
H	4.17816200	-1.84558200	8.62794500
H	6.42099500	-2.93384500	8.76406900
H	7.99701600	-2.71466300	6.83611500
H	9.38649400	-2.41903900	4.80512700
H	12.09526200	-2.78372200	2.30638300
H	11.50537400	-2.10643800	3.82591000
H	10.71796800	-3.53744700	3.11611000
H	11.96028100	-0.58597300	1.24549500
H	10.47356700	0.35510600	1.14996600
H	11.29893900	0.16615300	2.70505800
H	10.84732700	-2.66975500	0.23814200
H	9.36079900	-3.31901500	0.94528900
H	9.33406300	-1.78771000	0.05286900
H	7.16479100	-0.94190800	0.56918200
H	8.52786300	0.17127900	0.70758100
H	6.49763200	1.27537900	0.05085700
H	5.60994200	0.74294000	1.41146800

[($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)]$^+$

Br	4.68476700	4.94739400	4.89158800
Zn	6.23634800	3.98429200	3.45322300
N	7.89094500	4.99188200	2.75382000
N	7.60318400	2.56764200	3.89476500
N	7.68795400	1.30197500	4.36085500
N	3.72436100	2.86625200	2.24781000
H	2.94694700	3.21689700	1.68414400
H	3.56405400	3.18079400	3.21439800
N	4.96318600	3.49488500	1.81383500
H	4.74028100	4.37017700	1.33527700
H	5.35458200	2.85911100	1.11292200
C	6.67349500	7.01386200	2.10560200
C	7.96067800	6.25425500	2.27456200
C	9.19550800	6.81685200	1.93736100
C	10.36021100	6.06990800	2.09502700
C	10.27950500	4.77265700	2.59583600
C	9.02569200	4.26059300	2.92259000
C	8.83618200	2.92076300	3.48902800
C	9.72562500	1.86654600	3.70965100
C	8.97355700	0.83514000	4.27376700
C	9.47075900	-0.54239600	4.70745000

C	10.99807700	-0.60476500	4.47830900
C	9.21535100	-0.78417900	6.21598500
C	8.82378300	-1.65729500	3.84762400
C	6.50650700	0.68176300	5.00164200
C	5.17629500	1.01101700	4.31788600
C	5.08070500	0.65135600	2.82643300
C	3.71938000	0.89504500	0.44224800
C	2.54002500	1.62853900	-0.25034600
C	1.14843600	1.37776700	0.37625700
C	1.11686300	1.37864600	1.92255000
C	2.29831600	0.64683000	2.61647700
C	2.25914700	-0.89361400	2.41665400
C	2.53330800	-1.38035100	0.97424000
C	3.67872000	-0.64600100	0.23749400
B	3.73240000	1.15503700	2.05123200
H	6.86423600	8.07478900	1.92879700
H	6.11206300	6.63769900	1.23927300
H	6.03668700	6.91802000	2.99169500
H	9.23278800	7.83163800	1.55708300
H	11.32447300	6.49682300	1.83682300
H	11.16988500	4.17254000	2.74355400
H	10.77950600	1.83812800	3.48619100
H	11.36776100	-1.58684300	4.78779900
H	11.25803600	-0.47325800	3.42240200
H	11.52902200	0.14997900	5.06845200
H	9.24596300	-2.62571800	4.13568700
H	7.73914200	-1.72671300	3.96918900
H	9.03240000	-1.50133700	2.78384100
H	9.67298600	0.00428400	6.82329200
H	8.15453900	-0.83780200	6.47240300
H	9.66832900	-1.73719300	6.50833500
H	6.67700000	-0.39196600	4.97985800
H	6.49218000	1.00416000	6.04917000
H	4.41094600	0.46367200	4.88188500
H	4.94667100	2.06642700	4.51140700
H	5.98894000	1.00216500	2.30655900
H	5.13381100	-0.44117600	2.73717500
H	2.18112700	0.82203100	3.69921100
H	4.64445100	1.23148700	-0.06924300
H	1.08281100	2.42371100	2.28077700
H	0.44320400	2.13034100	-0.00042300
H	0.15920300	0.95264300	2.25284500
H	0.76587400	0.42141800	0.01168600
H	3.00319400	-1.34272000	3.08959400
H	1.28811200	-1.29182700	2.74420400
H	2.76388000	-2.45334100	0.99972000
H	1.61514300	-1.30250200	0.38480300
H	3.61738300	-0.88239200	-0.83459100

H	4.63980800	-1.05669800	0.57533100
H	2.74090100	2.71835500	-0.25240900
H	2.49985800	1.36753300	-1.31723300

[($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(N_2H_4)]$^+$

Br	4.48748100	5.96345300	2.88652300
Zn	2.43639900	5.89784700	3.97737900
C	2.77114100	2.64035200	4.72004200
C	1.41233900	2.98323900	4.17046500
C	0.43282000	2.00340500	3.98319000
C	-0.81524700	2.36373900	3.48133100
C	-1.06401900	3.69531700	3.15778600
C	-0.04991200	4.63075900	3.35298500
C	-0.18909200	6.04396900	2.98704100
C	-1.18804900	6.73396800	2.29609800
C	-0.72707000	8.04294500	2.14445000
C	-1.40626200	9.17374600	1.37216800
C	-1.57942800	10.45489200	2.22196700
C	-0.60643900	9.48307000	0.08065900
C	-2.81621200	8.69886300	0.95262200
C	1.43301500	9.21440700	2.94777000
C	1.27535500	9.93247400	4.30046800
C	1.85858700	9.18958900	5.51484500
C	3.40081300	9.18513600	5.57909500
C	3.39742700	8.27309200	8.23553900
C	3.36281900	9.71781100	8.81137400
C	4.73299300	10.42679600	8.90939600
C	5.65296600	10.23576800	7.68229100
C	5.68336500	8.79777400	7.09572300
C	6.39096500	7.79002600	8.04312300
C	5.62459600	7.44854300	9.34332200
C	4.09865400	7.25721500	9.17711600
B	4.14143600	8.36525100	6.78884700
N	1.16000400	4.27508600	3.86411500
N	0.82738100	6.87922800	3.26654900
N	0.50076300	8.08739800	2.75361400
N	4.27404700	6.75823400	6.19960600
N	3.00011800	6.07181100	6.01464800
H	-0.63191600	10.94062300	2.46582100
H	-2.17562500	11.17876100	1.65697300
H	-2.10972500	10.24400300	3.15710400
H	-2.77429600	7.82781000	0.29022900
H	-3.43675600	8.45149600	1.82090700
H	-3.31699500	9.50210100	0.40413600
H	0.39904600	9.86598500	0.27969200
H	-0.50832600	8.58934800	-0.54442200

H	-1.13680800	10.24544800	-0.49967300
H	-2.11721300	6.33881300	1.91953300
H	-1.58521100	1.61249800	3.33481800
H	-2.02170000	4.00462400	2.75535100
H	0.65716600	0.97094300	4.22755200
H	3.56129500	3.20030700	4.20836300
H	2.82459000	2.85833200	5.79617000
H	2.98088600	1.57409000	4.60593700
H	2.44060300	8.80796200	2.82356500
H	1.26316800	9.90359900	2.12284600
H	1.78062900	10.90225400	4.20194500
H	0.21307600	10.14973700	4.45997100
H	1.46554800	9.66815300	6.41944400
H	1.43464200	8.17368900	5.52783200
H	3.81435000	8.85625800	4.60926600
H	3.70850800	10.23752100	5.64799200
H	2.33473200	7.96164300	8.17838600
H	6.29157600	8.85181500	6.17722400
H	3.63224600	7.27014800	10.17248700
H	3.90732500	6.23183400	8.80355300
H	6.05414300	6.54212100	9.79063500
H	5.80117400	8.23810100	10.07746200
H	6.60197000	6.85438100	7.49175800
H	7.38934700	8.16113400	8.31369300
H	5.33172700	10.92317900	6.88882500
H	6.67091600	10.55310100	7.95062000
H	4.56104500	11.50036600	9.06121100
H	5.25159800	10.09276800	9.81285900
H	2.70394300	10.32084900	8.17140500
H	2.89193500	9.71710000	9.80520300
H	4.75006300	6.73505600	5.28547100
H	4.84790500	6.23492800	6.86359300
H	2.33972900	6.57794400	6.61190000
H	3.07482100	5.12908300	6.40188900

($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NH_2NH)

C	3.31027800	-0.15872200	6.56443800
C	4.59408100	-0.93091400	6.68057200
C	4.93773000	-1.65472300	7.82867500
C	6.14674700	-2.34508300	7.86612000
C	6.99834400	-2.29692800	6.76565200
C	6.60101000	-1.55608600	5.65069200
C	7.42695600	-1.42017600	4.44567800
C	8.71116300	-1.88810500	4.13452700
C	8.98996500	-1.42263800	2.85164600
C	10.25718100	-1.66437100	2.03436100

C	11.18222000	-2.61048400	2.83253600
C	9.93724400	-2.35592300	0.68676600
C	11.03147200	-0.34462200	1.79888300
C	7.57683800	-0.09990400	1.13734600
C	6.60177500	1.08676100	1.13091600
C	8.51718500	3.02357300	1.75368900
C	8.86277800	3.21777800	0.25409700
C	7.93005200	4.18064000	-0.51550600
C	6.42385000	4.01037600	-0.20815800
C	6.07050100	3.77342000	1.28318700
C	6.28473200	5.04124900	2.15132100
C	7.76047500	5.46735200	2.34311800
C	8.75727000	4.30838400	2.59221600
B	6.95947700	2.52078900	1.86140900
N	5.41955600	-0.90026400	5.61795000
N	6.94105000	-0.71087900	3.41628200
N	7.88946300	-0.69862600	2.46090000
N	6.60744600	2.35192800	3.46565000
N	5.26174600	1.95098700	3.88712200
Zn	4.98650600	0.05040300	3.75629900
Br	3.20145300	-1.12807100	2.78986800
H	4.98759800	3.55904500	1.30428500
H	9.22914100	2.27140200	2.14151100
H	5.73154500	5.89491400	1.72996400
H	5.82555300	4.87557200	3.13980300
H	8.08354100	6.03024200	1.46243600
H	7.82556000	6.18083200	3.17711600
H	5.88802700	4.89227200	-0.59325600
H	6.04116200	3.16203600	-0.79172500
H	8.23109700	5.21254700	-0.30805000
H	8.09287600	4.04764200	-1.59452300
H	9.90083900	3.56954500	0.13852900
H	8.82762600	2.23525500	-0.24019500
H	8.72880300	4.04070500	3.66208300
H	9.77905700	4.68776800	2.43257200
H	3.52119200	0.88725500	6.31218500
H	2.69456000	-0.56924400	5.75506300
H	2.74028800	-0.19020400	7.49669900
H	4.25995600	-1.66970200	8.67553400
H	6.42628500	-2.91412600	8.74824600
H	7.94842500	-2.81963900	6.76700100
H	9.36175200	-2.48146500	4.75649600
H	12.09309900	-2.79897800	2.25492800
H	11.48251200	-2.17176700	3.79035500

H	10.70306800	-3.57629200	3.02675700
H	11.96276800	-0.55791200	1.26152000
H	10.46972300	0.38342600	1.20844000
H	11.29156300	0.12899500	2.75184000
H	10.87364700	-2.60411900	0.17432000
H	9.38286900	-3.28745000	0.84646600
H	9.35259700	-1.72501800	0.01380100
H	7.18657400	-0.91956200	0.52065000
H	8.53363900	0.20544400	0.71655500
H	6.48016000	1.28493500	0.05767600
H	5.60933200	0.72621500	1.43215600
H	6.82820200	3.22434200	3.95047700
H	7.24584000	1.66340400	3.86741100
H	4.64670200	2.46748000	3.25901400

($^{2\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NHNH$_2$)

C	3.26247100	-0.20662300	6.56576500
C	4.55316800	-0.97132200	6.66654300
C	4.87935500	-1.72753400	7.79723900
C	6.09096500	-2.41386100	7.83788300
C	6.95770600	-2.33606500	6.75244500
C	6.57927300	-1.56675400	5.65029800
C	7.41689300	-1.42214900	4.45722900
C	8.71522200	-1.85290700	4.16183900
C	8.99218200	-1.38468000	2.87755400
C	10.27100300	-1.60312200	2.07170600
C	11.20577200	-2.53091100	2.88019900
C	9.97207700	-2.30429600	0.72416400
C	11.02334500	-0.27074100	1.83820900
C	7.56403100	-0.08924500	1.14805000
C	6.59090600	1.09696100	1.15360000
C	8.53707800	3.01680300	1.70221700
C	8.82922800	3.17752400	0.18914100
C	7.87656000	4.13239800	-0.56607100
C	6.38123400	3.98887100	-0.19740800
C	6.08595500	3.79055800	1.31115800
C	6.35004300	5.06769600	2.14836000
C	7.83642000	5.47483500	2.26913900
C	8.81595600	4.30451800	2.51910300
B	6.98089100	2.53852200	1.92205000
N	5.39838600	-0.90161700	5.61810200
N	6.92295600	-0.73614500	3.41485500
N	7.87715300	-0.69640200	2.47081000

N	6.72703200	2.45568100	3.48668500
N	5.34873300	2.00195900	3.77188700
H	4.77759700	2.42523800	3.03542800
H	5.05028600	2.47118500	4.62906600
Zn	5.04766500	0.01507400	3.72585800
Br	3.11379600	-0.89759300	2.78237700
H	4.99154100	3.60943800	1.36460500
H	9.25470900	2.26299400	2.07891900
H	5.78605300	5.92394100	1.74181300
H	5.96201400	4.89715800	3.16110200
H	8.13733000	6.01667700	1.36578700
H	7.94021300	6.20434700	3.08599800
H	5.84460000	4.87121300	-0.58274700
H	5.96443700	3.13521400	-0.75037800
H	8.19510100	5.16477100	-0.39077100
H	7.99551200	3.97593600	-1.64845200
H	9.86454700	3.52079600	0.02553000
H	8.77099500	2.18689500	-0.28936300
H	8.76429900	4.03961100	3.58259900
H	9.84317000	4.66541000	2.33928200
H	3.45608200	0.87140800	6.49928500
H	2.71507500	-0.49739600	5.66175500
H	2.62988000	-0.38202900	7.43950000
H	4.18545600	-1.77098100	8.62970900
H	6.35694200	-3.00626100	8.70854900
H	7.90548500	-2.86250100	6.75036200
H	9.37897800	-2.41992500	4.79413100
H	12.12348700	-2.70519200	2.30924600
H	11.49299500	-2.08324300	3.83793600
H	10.74278800	-3.50476700	3.07465100
H	11.96250300	-0.47188200	1.30997000
H	10.45461800	0.44618700	1.24192800
H	11.26649500	0.21144200	2.79106600
H	10.91658100	-2.53435700	0.21842600
H	9.43592500	-3.24691700	0.88224300
H	9.37943500	-1.68603300	0.04666200
H	7.18814000	-0.91412200	0.52784600
H	8.52099000	0.22752700	0.73774200
H	6.47053400	1.29955100	0.08072900
H	5.59237600	0.71879600	1.43235400
H	7.31706600	1.72319800	3.88392300

($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NH_2NH)

Br	5.26942200	5.23590500	5.37048800
Zn	6.12626500	4.01533300	3.57244600
N	7.83223100	4.96845500	2.72603500
N	7.56318600	2.59227400	3.94850200
N	7.64095200	1.34171800	4.43636300
N	3.60053900	2.84704300	2.35899300
N	4.86595700	3.55461600	2.06559200
H	4.60778800	4.40231000	1.55589200
H	5.33410000	2.96789200	1.36945400
C	6.61422700	6.98923300	2.11137000
C	7.89655600	6.20823300	2.19949900
C	9.11505400	6.73179800	1.75438600
C	10.27169500	5.96242500	1.85810000
C	10.19785600	4.68755300	2.41085400
C	8.95548300	4.21919400	2.84226400
C	8.77298800	2.90255600	3.45940600
C	9.64838800	1.82566500	3.64802900
C	8.90268400	0.83050900	4.27755600
C	9.37361900	-0.55800300	4.70014900
C	10.88434400	-0.67702100	4.39869600
C	9.18541400	-0.77944300	6.22110700
C	8.64705700	-1.65663100	3.88450800
C	6.45252400	0.76838700	5.10819400
C	5.13843900	1.07678600	4.38244800
C	5.06565100	0.68017600	2.90339500
C	3.81898600	1.00388800	0.47883600
C	2.64002400	1.69586200	-0.24783800
C	1.23598100	1.33817700	0.29111000
C	1.12532700	1.29229200	1.83226800
C	2.30615400	0.59983900	2.55875400
C	2.36590000	-0.92795900	2.31095000
C	2.75486300	-1.35076900	0.87370000
C	3.89133700	-0.52303500	0.22659700
B	3.72720400	1.28545100	2.10147500
H	6.79894900	8.01661500	1.78800400
H	5.92884800	6.52944800	1.38807200
H	6.10686900	7.00629900	3.08277100
H	9.14602000	7.73128600	1.33430700
H	11.22457500	6.35566000	1.51603500
H	11.08166200	4.06867800	2.51716900
H	10.68420800	1.76209600	3.35666300
H	11.23666400	-1.66845800	4.70111400
H	11.09464000	-0.56316800	3.32975500
H	11.46783900	0.06791200	4.95095300

H	9.03179500	-2.64103900	4.17419500
H	7.56506200	-1.66512500	4.03835500
H	8.82515200	-1.52382600	2.81212100
H	9.70805100	-0.00652200	6.79559000
H	8.13725700	-0.77655200	6.52894300
H	9.60704200	-1.75117100	6.50145000
H	6.61109200	-0.30678100	5.14662700
H	6.44286000	1.15213000	6.13613700
H	4.35506000	0.55919400	4.95177600
H	4.90973100	2.14153700	4.52530600
H	5.99052900	1.01506500	2.39839600
H	5.10749100	-0.41623600	2.84145100
H	2.11676200	0.72793200	3.64128800
H	4.74582200	1.41777600	0.02426800
H	1.06515200	2.32431000	2.20071300
H	0.51001300	2.06830500	-0.09690900
H	0.16744600	0.81323200	2.09789300
H	0.92132000	0.37541500	-0.12700700
H	3.09392100	-1.36267700	3.01193800
H	1.40142400	-1.40132800	2.56015700
H	3.04439500	-2.41258200	0.87757400
H	1.86788900	-1.30106000	0.23368300
H	3.90492600	-0.74249200	-0.85443700
H	4.85448900	-0.88807200	0.61223000
H	2.77440900	2.78130500	-0.14468700
H	2.66395800	1.48282800	-1.33052500
H	3.42373200	3.04239100	3.34528200

($^{3\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NHNH$_2$)

Br	5.12924500	4.97628300	5.34824100
Zn	6.12468800	4.01404600	3.43403400
N	7.86091700	4.97754200	2.77543200
N	7.60309400	2.58087700	3.94757900
N	7.69065900	1.31522200	4.39294600
N	3.75766000	2.88321200	2.26189400
H	2.99668100	3.29600000	1.71788300
H	3.52262000	3.10500000	3.23337900
N	4.97501700	3.62643300	1.94406800
C	6.57551700	6.91550100	2.07791000
C	7.89346200	6.21068900	2.23416900
C	9.11094600	6.78159500	1.84607700
C	10.29180800	6.06492900	2.02706100
C	10.24480000	4.79115000	2.58761200

C	9.00168300	4.27177700	2.95332900
C	8.82749900	2.93836500	3.53922100
C	9.72539300	1.87901100	3.74075000
C	8.97727200	0.84294300	4.29210300
C	9.46505400	-0.54590400	4.69460000
C	10.99187900	-0.61520300	4.46817000
C	9.20635500	-0.82472700	6.19552600
C	8.81348700	-1.63790500	3.80999500
C	6.50006800	0.69251300	5.01355200
C	5.17564900	1.03897500	4.32244000
C	5.07414200	0.67203900	2.83406700
C	3.75030000	0.92627500	0.43934600
C	2.58255800	1.65136800	-0.27773900
C	1.17984000	1.40299000	0.32668800
C	1.12155700	1.40876000	1.87314300
C	2.29800700	0.69137700	2.58801900
C	2.26442800	-0.84754800	2.40294000
C	2.56235900	-1.34631300	0.96887600
C	3.71618600	-0.61217700	0.24460800
B	3.74550300	1.23896800	2.04755100
H	6.68871000	7.85437900	1.52964000
H	5.85919400	6.27144800	1.55417900
H	6.14417300	7.13110400	3.06335700
H	9.12178100	7.77425600	1.40893000
H	11.24441600	6.49592900	1.73235700
H	11.14775400	4.21107600	2.74231600
H	10.77674100	1.85482900	3.50338900
H	11.35715500	-1.60619600	4.75704900
H	11.25273200	-0.45931000	3.41583100
H	11.52434400	0.12714900	5.07274100
H	9.21670800	-2.61995400	4.08266700
H	7.72655600	-1.68658000	3.91616900
H	9.03433400	-1.46131000	2.75188500
H	9.67396300	-0.05607100	6.82082200
H	8.14391500	-0.86257600	6.44718600
H	9.64280600	-1.79257800	6.46725600
H	6.66219500	-0.38323000	4.98090500
H	6.47853400	1.00469500	6.06477900
H	4.40140800	0.51092600	4.89527000
H	4.97635400	2.10115700	4.50361600
H	5.97734400	1.02818000	2.31582600
H	5.11493600	-0.42335300	2.75359700
H	2.15823400	0.87460800	3.66889300
H	4.67897400	1.27152700	-0.05096400

H	1.08220800	2.45459800	2.22138600
H	0.48033100	2.15694900	-0.06245700
H	0.15742100	0.97773100	2.18649100
H	0.79912900	0.44510900	-0.04062200
H	3.00294200	-1.28782900	3.08803900
H	1.28977100	-1.25442200	2.71773900
H	2.79082600	-2.42141900	1.00517100
H	1.65168300	-1.27077600	0.36561400
H	3.67059200	-0.86577400	-0.82700400
H	4.67153700	-1.01984300	0.60325300
H	2.78752000	2.73514900	-0.27389700
H	2.55359600	1.37951400	-1.34497400
H	5.40653900	3.07959000	1.20045600

($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NH_2NH)

Br	4.25905600	6.10945000	2.53191600
Zn	2.47816400	5.91533300	4.08468600
C	2.75998700	2.74012700	4.81745400
C	1.40060200	3.02512700	4.24544600
C	0.42090800	2.03485800	4.09966900
C	-0.81465600	2.36606500	3.54976500
C	-1.06026700	3.67855200	3.15384300
C	-0.04695800	4.62253400	3.32364300
C	-0.18806900	6.03088500	2.93982700
C	-1.17649500	6.71532500	2.21763900
C	-0.72997400	8.02956500	2.10279300
C	-1.39274300	9.16859400	1.33118100
C	-1.61228700	10.42615300	2.20468900
C	-0.55487900	9.52282200	0.07677800
C	-2.78092500	8.69114300	0.84875900
C	1.39975800	9.20350200	2.99872700
C	1.21780600	9.89179900	4.36573000
C	1.83340500	9.15167000	5.56793000
C	3.37432900	9.18565600	5.61970800
C	3.41768000	8.22242300	8.25112700
C	3.37783700	9.65557300	8.84456800
C	4.74107200	10.37921000	8.93280700
C	5.64299300	10.21199300	7.68863600
C	5.67813300	8.78261600	7.09022600
C	6.41494500	7.77974700	8.01928800
C	5.66438700	7.40311100	9.32048800
C	4.13780000	7.19878200	9.16681800
B	4.13548100	8.29824700	6.78208200
N	1.15190600	4.29156000	3.85772900

N	0.79999500	6.87379200	3.26534600
N	0.47626800	8.07849700	2.75966500
N	4.25874100	6.76842900	6.15731200
N	3.04835200	5.98718300	5.91307800
H	-0.67799300	10.89893800	2.51501200
H	-2.18025300	11.16873900	1.63295500
H	-2.18610600	10.18466100	3.10619600
H	-2.70318100	7.83373700	0.17182900
H	-3.42686600	8.41403300	1.68913300
H	-3.27279300	9.50117400	0.30038900
H	0.43944600	9.90566600	0.32406200
H	-0.42402900	8.64482600	-0.56461900
H	-1.07085200	10.29606600	-0.50397000
H	-2.08487400	6.30859300	1.80355300
H	-1.58354000	1.60769200	3.43253100
H	-2.01505800	3.96968400	2.73022400
H	0.63683300	1.01985500	4.41560300
H	3.52246300	2.81747400	4.03187300
H	3.01182300	3.48737300	5.58056000
H	2.80633600	1.73584000	5.24696400
H	2.40887200	8.79757800	2.88762300
H	1.24510300	9.91161500	2.18585500
H	1.68652400	10.88244200	4.28157800
H	0.14631000	10.06731900	4.52730500
H	1.43181100	9.61257100	6.47962800
H	1.46468300	8.11954700	5.57775800
H	3.77757000	8.88677400	4.63532100
H	3.66316700	10.24314100	5.71493900
H	2.36367800	7.89476300	8.19462400
H	6.27866200	8.85091900	6.16532100
H	3.68808100	7.19100000	10.17285100
H	3.95066700	6.18890400	8.76607700
H	6.10934100	6.48962300	9.74151700
H	5.84448200	8.17842000	10.07132200
H	6.62980900	6.85727200	7.45382500
H	7.40954800	8.16711800	8.29195100
H	5.29550400	10.90292200	6.90885300
H	6.66094500	10.54652800	7.94662000
H	4.56465500	11.45080700	9.10626000
H	5.27889600	10.03279600	9.82154300
H	2.70661000	10.26150100	8.21920000
H	2.92167100	9.64696700	9.84807300
H	4.86787900	6.20371000	6.75262600
H	4.75020200	6.83276900	5.25911800

H	2.37944100	6.34013700	6.59347200

($^{4\text{-BBN}}$NN$^{t\text{Bu}}$)ZnBr(NHNH$_2$)

Br	4.25954500	5.82251300	2.46199500
Zn	2.52928400	5.91440100	4.02135900
C	2.82047300	2.65052000	4.67410400
C	1.43736100	2.99177700	4.18995300
C	0.44179500	2.01879200	4.04967200
C	-0.82044000	2.38910500	3.59165800
C	-1.06614100	3.71913900	3.26362100
C	-0.03179000	4.64439000	3.41341200
C	-0.16579400	6.05510200	3.03883800
C	-1.17196200	6.74171300	2.34727000
C	-0.70580800	8.04343600	2.17622100
C	-1.37742300	9.16614500	1.38688900
C	-1.53527800	10.46686800	2.20831700
C	-0.58235500	9.44439600	0.08601900
C	-2.79384100	8.69913000	0.98188700
C	1.46844300	9.21069900	2.95797700
C	1.30383700	9.95201300	4.29687800
C	1.87144000	9.21118100	5.52170100
C	3.41241800	9.16898000	5.59284000
C	3.38102700	8.24135200	8.23685300
C	3.33075700	9.69003400	8.78743200
C	4.69668100	10.40464100	8.89951600
C	5.63438000	10.20090400	7.68769200
C	5.67430900	8.76005700	7.12299200
C	6.37107100	7.75857100	8.07879500
C	5.59434800	7.43746900	9.37740200
C	4.07042800	7.24183800	9.19929700
B	4.15005600	8.23738600	6.77579000
N	1.18608500	4.28061300	3.88366500
N	0.85454000	6.88704100	3.29665900
N	0.52894600	8.08688800	2.77531500
N	4.31912300	6.74155400	6.26062200
N	3.01552400	6.10578800	5.95629600
H	-0.58054300	10.93903800	2.44828100
H	-2.11977700	11.18918600	1.62772700
H	-2.06828300	10.28025900	3.14699800
H	-2.76248100	7.81383300	0.33791600
H	-3.41043700	8.47178400	1.85851400
H	-3.29086600	9.49687200	0.42073700
H	0.42943500	9.81326600	0.27751800

H	-0.49796300	8.53717000	-0.52164000
H	-1.10355200	10.20470500	-0.50668600
H	-2.10441500	6.34275600	1.98259900
H	-1.60460000	1.64552300	3.48331000
H	-2.03493800	4.03740200	2.89542500
H	0.66490800	0.98628400	4.29586400
H	3.57995600	3.12530300	4.04320300
H	2.97478000	3.00087500	5.70239100
H	2.98313200	1.56982900	4.66823300
H	2.47282300	8.78938000	2.86377300
H	1.31860400	9.88284900	2.11401000
H	1.82883300	10.91103400	4.18886100
H	0.24144400	10.18864900	4.43932000
H	1.48383600	9.70942700	6.41879900
H	1.41964800	8.20829000	5.54408700
H	3.81290200	8.83507100	4.61649200
H	3.73420500	10.21943900	5.66703800
H	2.31862200	7.91968800	8.17765000
H	6.29792600	8.80447400	6.21107000
H	3.59689500	7.26454400	10.19631700
H	3.90387100	6.22819500	8.80724200
H	6.01714200	6.52843300	9.83152100
H	5.77086900	8.22933300	10.11382700
H	6.52043600	6.82131800	7.52966100
H	7.37604300	8.11919500	8.35815100
H	5.31802100	10.88186400	6.88479000
H	6.64627000	10.53488800	7.97254800
H	4.52361700	11.48170300	9.04583500
H	5.20323500	10.07157000	9.81128600
H	2.68599800	10.28737100	8.12596300
H	2.84335000	9.71589500	9.77698100
H	2.32012300	6.64717700	6.47592900
H	3.02351900	5.19568500	6.42158200
H	4.80118400	6.75841200	5.35979200

Pyridine

C	-2.33899300	-0.68746900	0.00002700
C	-0.94259100	-0.69301000	-0.00006900
C	-0.27421200	0.53126300	-0.00028400
C	-1.03002300	1.70357300	-0.00040600
C	-2.42230300	1.59628500	-0.00031500
N	-3.07878900	0.42893800	-0.00009100
H	0.81192000	0.57086200	-0.00035200

H	-2.89233000	-1.62554000	0.00018300
H	-0.39850300	-1.63292200	0.00004100
H	-0.55590500	2.68065000	-0.00054800
H	-3.04252300	2.49154100	-0.00037600

Pyridinium

C	-2.57110400	-0.73236500	0.00001300
C	-1.18675400	-0.70557000	-0.00005900
C	-0.53018300	0.53003400	-0.00025200
C	-1.27129000	1.71707100	-0.00039200
C	-2.65399000	1.64751000	-0.00032100
N	-3.25489800	0.43507300	-0.00011600
H	0.55478500	0.56777800	-0.00032300
H	-3.15885000	-1.64272000	0.00016900
H	-0.63606600	-1.63941400	0.00003900
H	-0.78687100	2.68694500	-0.00055500
H	-3.30396000	2.51452000	-0.00041000
H	-4.27229500	0.39960400	-0.00006900

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