Supporting information

to the manuscript

Neutral and anionic zinc compounds supported by a bis(imino)phenyl NCN ligand

by

Minh Tho Nguyen[†], Bullat Gabidullin[‡], Georgii Nikonov[†]*

[†]Department of Chemistry, Brock University, 1812 Sir Isaac Brock Way, St. Catharines, Ontario L2S 3A1, Canada

[‡]X-ray Core Facility, Faculty of Science, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada

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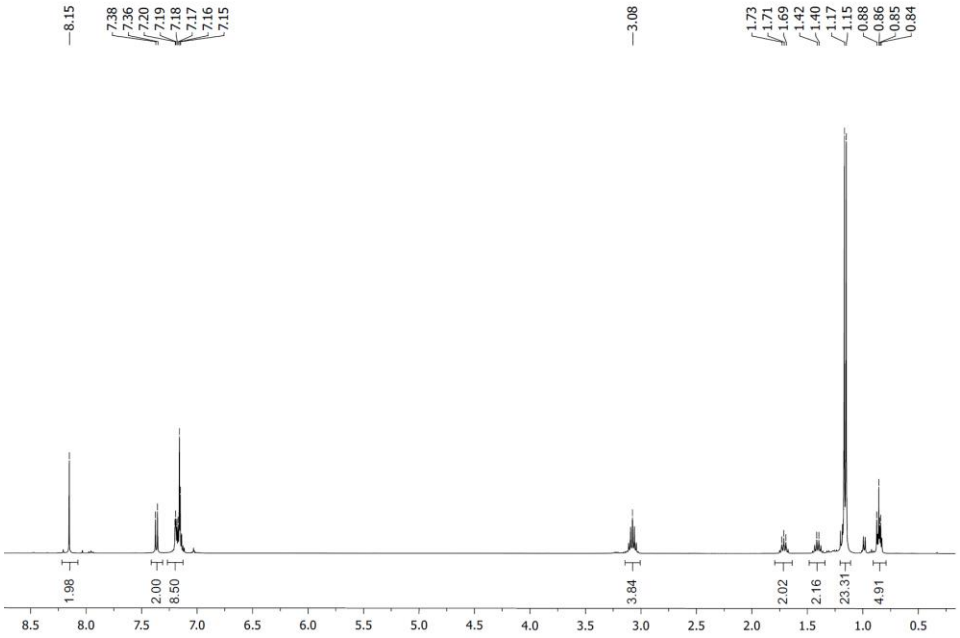
I. General information

All experiments involving air and moisture – sensitive compounds were carried out under an atmosphere of dried and purified nitrogen gas using standard Schlenk line or glovebox technique. THF, diethyl ether, benzene, DCM were purified by distillation over potassium hydroxide/benzophenone. Toluene, hexane, were purified by using Grubbs-type solvent purification system. All solvents were stored under nitrogen atmosphere prior to use. ^{1}H, ^{2}H, ^{13}C, ^{11}B spectra were recorded on Bruker DPX-300 and Avance III HD 400 MHz spectrometer. The chemical shifts are expressed in parts per million (ppm) with residual solvent signal as internal standard. The coupling constants (J) are reported in Hertz (Hz) and splitting patterns are indicated in singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (b). Unless indicated, starting materials were obtained from commercial sources. Bis(amino)aryl NCN pincer compound 2,6-(2,6-$^{i}Pr_2C_6H_3N{=}CH)C_6H_3$-1-Br was prepared according to literature procedure[1].

II. NMR Characterization of compounds

1. Compound 6

^{1}H NMR spectrum



$^{13}C\{^{1}H\}$ NMR spectrum

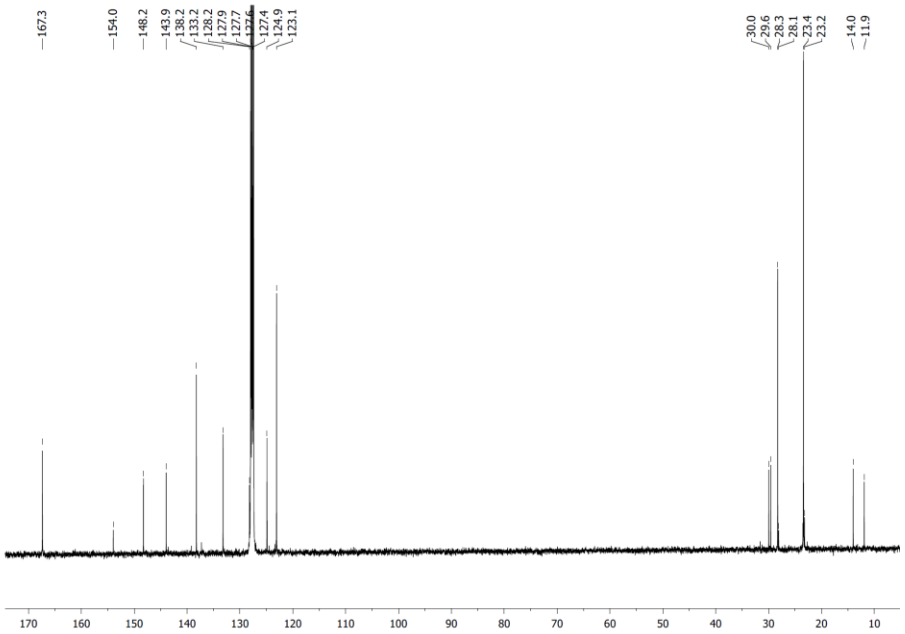
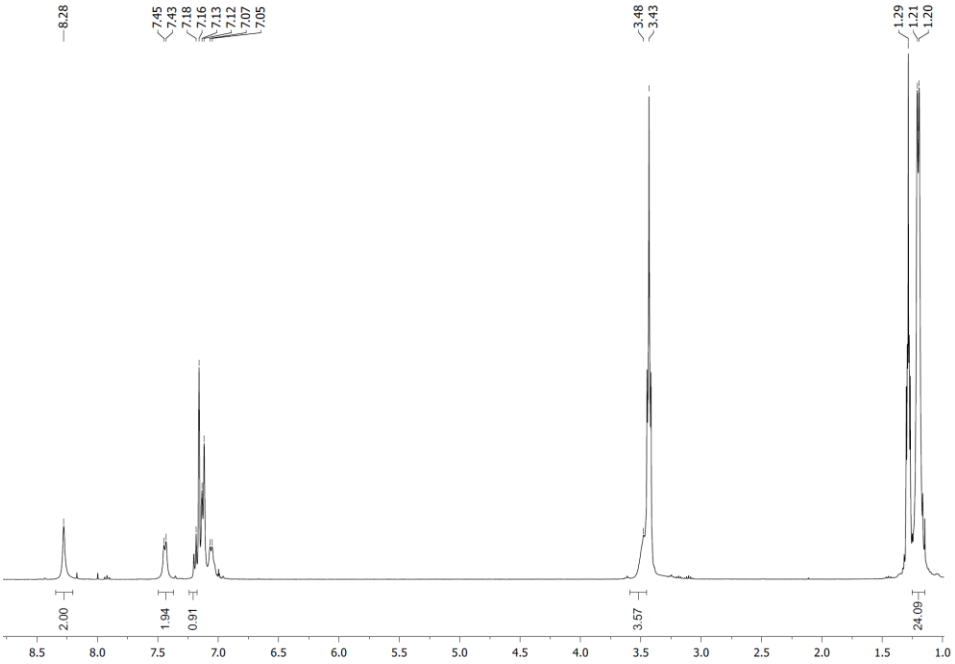


Figure SI1. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **6**

2. Compound 7

^{1}H NMR spectrum



$^{13}C\{^{1}H\}$ NMR spectrum

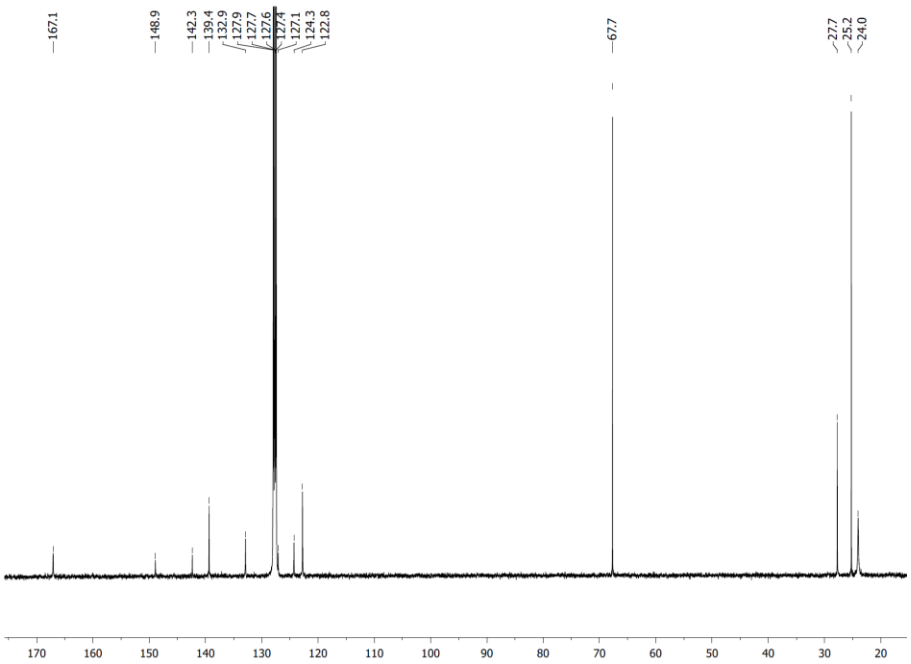
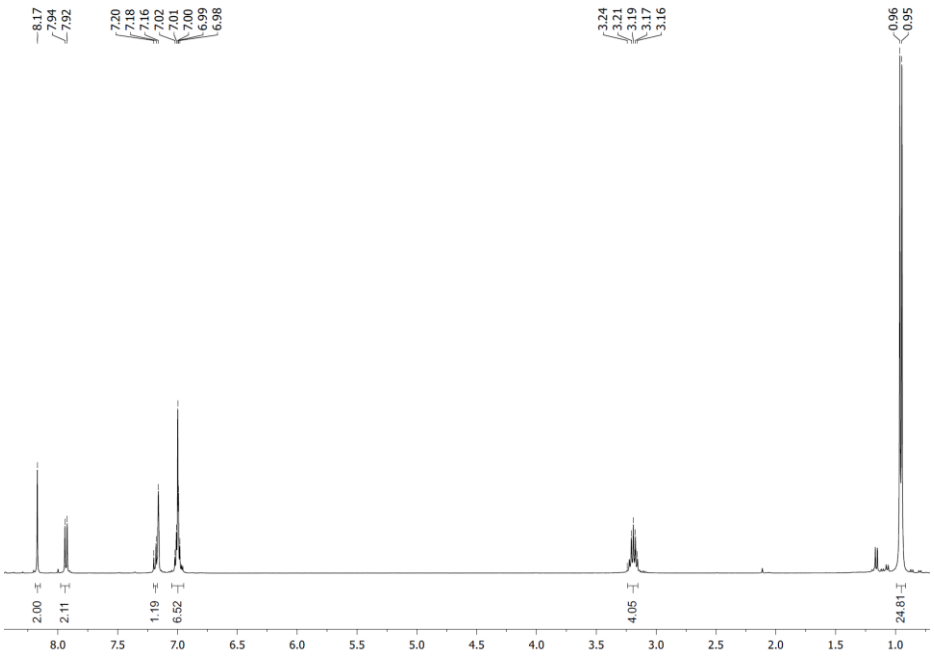


Figure SI2. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **7**

3. Compound 8

^{1}H NMR spectrum



$^{13}C\{^{1}H\}$ NMR spectrum

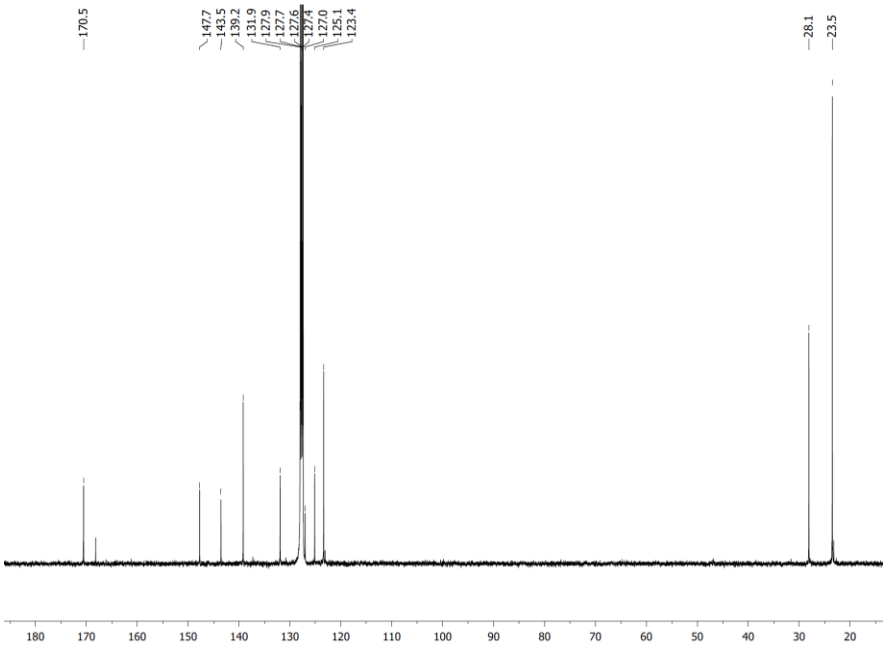
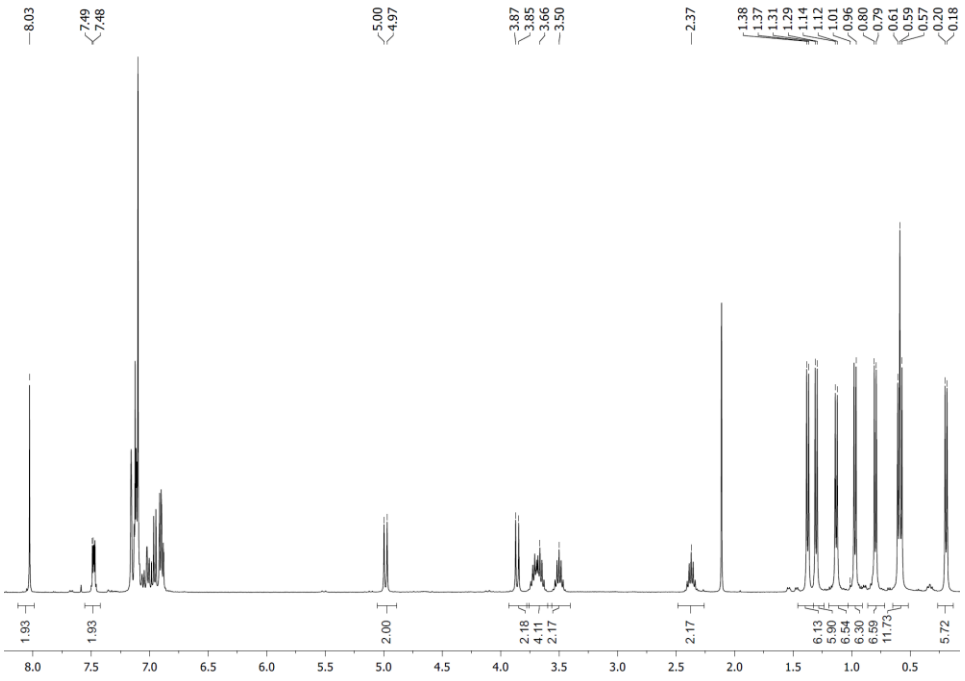


Figure SI3. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **8**

4. Compound 9

^{1}H NMR spectrum



$^{13}C\{^{1}H\}$ NMR spectrum

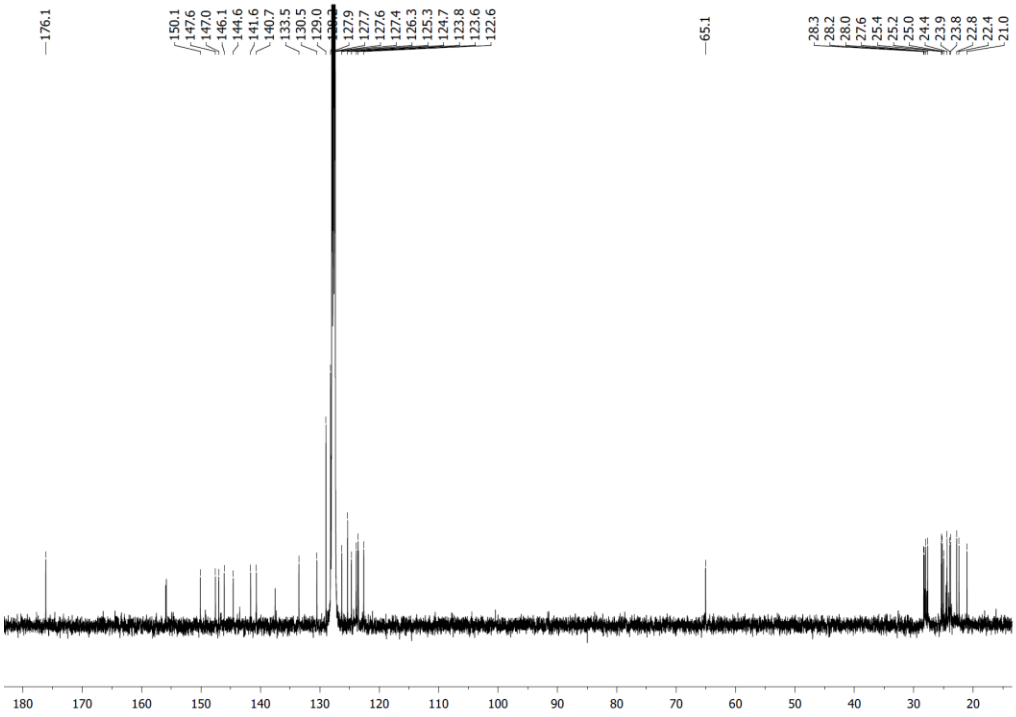


Figure SI4. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **9**

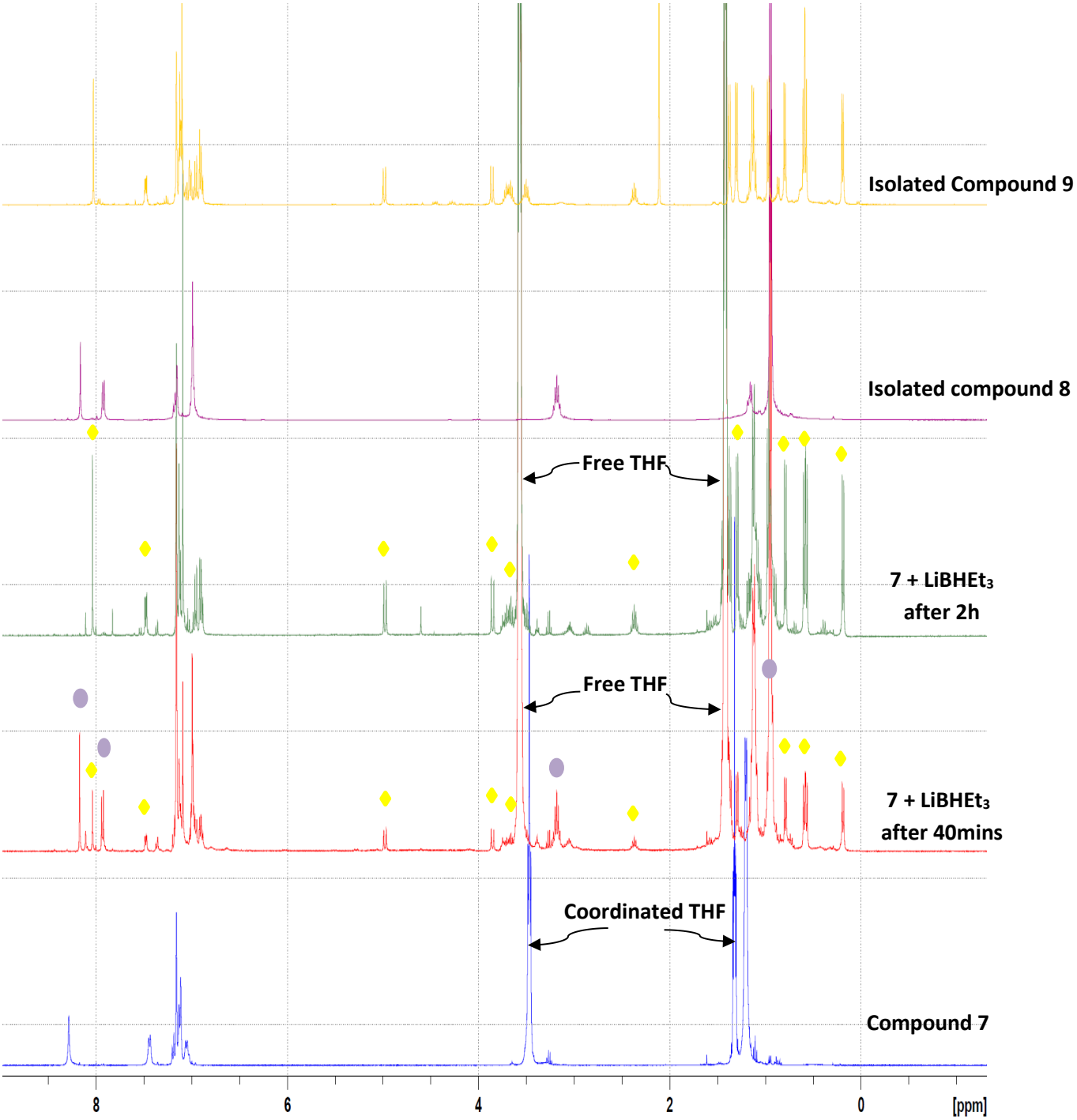


Figure SI5. ^{1}H NMR spectrum of the reaction between **7** + (superhydride) $LiBHEt_3$ at various time (yellow diamond corresponding to compound **9**, purple cycle corresponding to compound **8**).

III. Crystallographic data

Table S1 Crystal and structure refinement data for **6-9**.

	6	**7**	**8**	**9**
Empirical formula	$C_{26}H_{48}N_4Zn$	$C_{48}H_{69}Cl_2LiN_2OZn$	$C_{64}H_{78}N_4Zn$	$C_{64}H_{80}N_4Zn_2$
Formula weight	574.1	881.26	968.67	1036.06
colour, habit	colorless, block	colorless, block	colorless, block	orange, block
Crystal size, mm^3	0.16x0.31x0.84	0.75x0.74x0.50	0.21x0.25x0.27	0.08x0.34x0.43
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/n$	Pnma	P-1	$P2_1/c$
Unit cell dimensions:				
a, Å	9.555(3)	21.774(3)	13.522(4)	21.465(2)
b, Å	23.515(9)	21.338(3)	14.632(4)	15.5065(14)
c, Å	15.776(6)	10.5392(13)	15.856(5)	19.1466(18)
α, °	90	90	77.163(4)	90
β, °	106.742(4)	90	86.790(4)	114.8170(10)
γ, °	90	90	67.573(4)	90
Volume, $Å^3$	3394(2)	4896.7(11)	2826.0(15)	5784.3(9)
Z	4	4	2	4
Density (calcd), g/cm^3	1.123	1.195	1.138	1.190
Absorption coefficient, mm^{-1}	0.747	0.652	0.476	0.870
F(000)	1232	1880	1040	2208
Temperature, K	200(2)	200(2)	238(2)	200(2)

2θ range for data collection, °	2.19 to 28.28	1.87 to 28.38	1.77 to 27.00	1.68 to 28.32
Reflections collected	39832	81417	26044	69330
Independent reflections	8256 [R(int) = 0.0590]	6269 [R(int) = 0.0590]	12176 [R(int) = 0.0600]	14211 [R(int) = 0.0594]
Data / restraints / parameters	8256 / 91 / 391	6269 / 418 / 439	12176 / 0 / 622	14211 / 0 / 631
Goodness-of-fit on F^2	1.010	1.028	0.956	1.020
Final R indices [I>2σ(I)]	R_1 = 0.0596, wR_2 = 0.1206	R_1 = 0.0539, wR_2 = 0.1413	R_1 = 0.0591, wR_2 = 0.1152	R_1 = 0.0508, wR_2 = 0.1316
R indices (all data)	R_1 = 0.1149, wR2 = 0.1402	R_1 = 0.0911, wR_2 = 0.1718	R_1 = 0.1243, wR_2 = 0.1400	R_1 = 0.1192, wR_2 = 0.1798
Largest diff. peak and hole, e.$Å^{-3}$	0.563 and -0.699	0.477 and -0.655	0.291 and -0.442	1.595 and -1.270

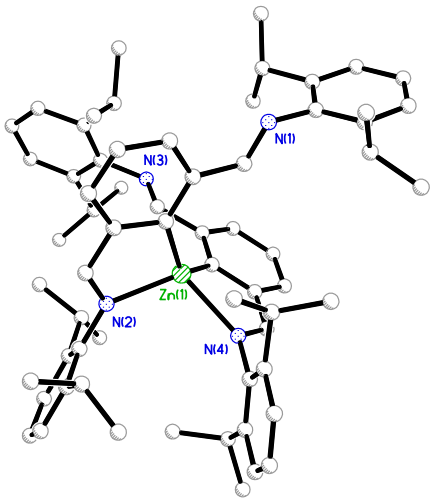


Figure SI6. Molecular structure of complex **8**

IV. Reference

1 S. Nückel and P. Burger, *Organometallics*, 2000, **19**, 3305–3311.