Supplementary Information for

Study of an S=1 Ni^{II} Pincer Electrocatalyst Precursor for Aqueous Hydrogen Production Based on Paramagnetic ^1H NMR

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S1: SQUID measurements

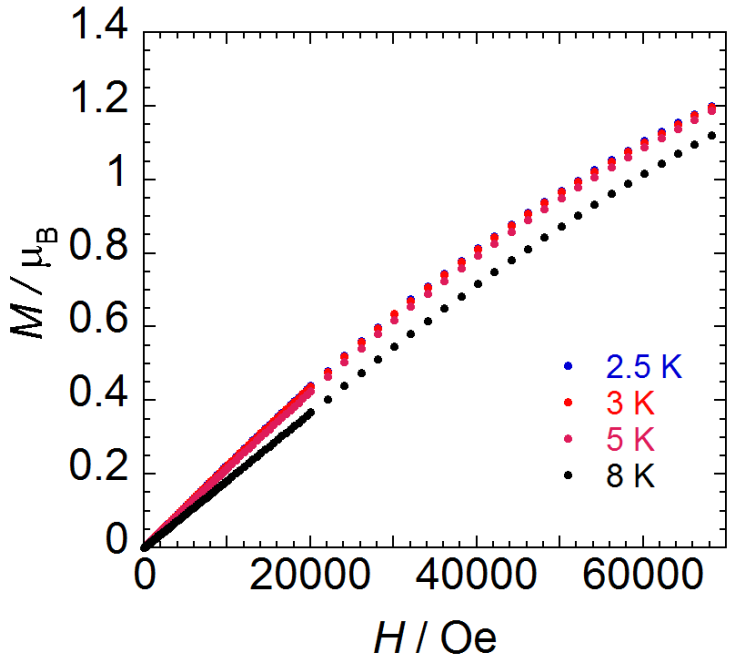


Figure S1-1. Magnetization plot, *M vs. H*, for NiNNN.

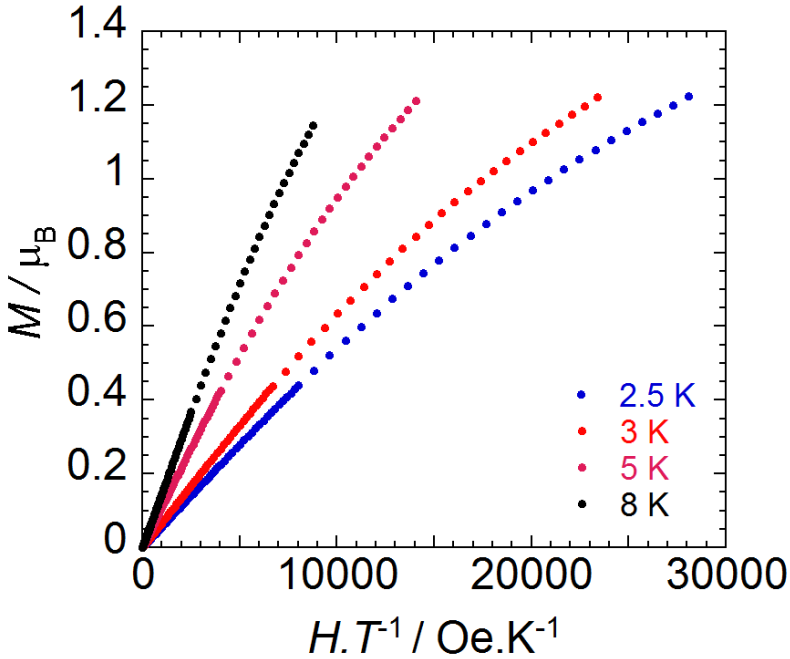


Figure S1-2. Magnetization plot, *M vs. H/T*, for NiNNN.

S2: Preparative experimental details

T1 Measurements

CD_2Cl_2 T1 data collected on a 500MHz Bruker instrument at -40°C. Data worked up using the Bruker Topspin T1/T2 relaxation module and MestReNova 5.2.4-3824.
d1=2s, SW=50, 64 scans per datapoint.

Stacked spectra available in S3.

Synthesis of Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (NNN) ligand

NNN ligand was prepared by a Schiff's base reaction using a modified literature methodology. 2,6-diacetylpyridine (0.443 g, 2.7 mmol) and p-toluenesulfonic acid (0.027 g, 0.2 mmol) were added to a 100 mL round bottom flask with a magnetic stir bar and toluene was added via syringe (10 mL) forming a heterogeneous solution. 2,6-dimethylaniline was purified by passing it through a column of basic alumina and then an aliquot was added via microsyringe to the reaction mixture (0.74 mL, 6.0 mmol), quickly forming a homogeneous yellow solution. The reaction mixture was stirred at reflux for 10 hours under nitrogen, and water that formed was removed with a Dean-Starke trap.

After cooling to room temperature, the brown reaction mixture was washed with a solution of $NaCO_3$ and then twice with water. The organic layer was separated and the combined aqueous layers were washed twice with diethyl ether. All organic layers were combined and dried with $MgSO_4$ and rotary evaporation of the resulting solution yielded a brown residue. After adding EtOH to the residue, the mixture was stored at -24 °C for 3 hr. The solid was isolated by vacuum filtration and washed several times with cold EtOH. The filtrate was stored overnight at -24 °C, and more yellow crystals were isolated and washed in the same manner. Overall yield: 0.485 mg (48.5 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 7.8 Hz, 2H), 7.92 (t, J = 7.8 Hz, 1H), 7.08 (d, J = 7.5 Hz, 4H), 6.99 – 6.90 (m, 2H), 2.24 (s, 6H), 2.06 (s, 12H).

Synthesis of **ZnNNN**

ZnNNN was prepared by a known synthesis for a zinc chloride analog[i]

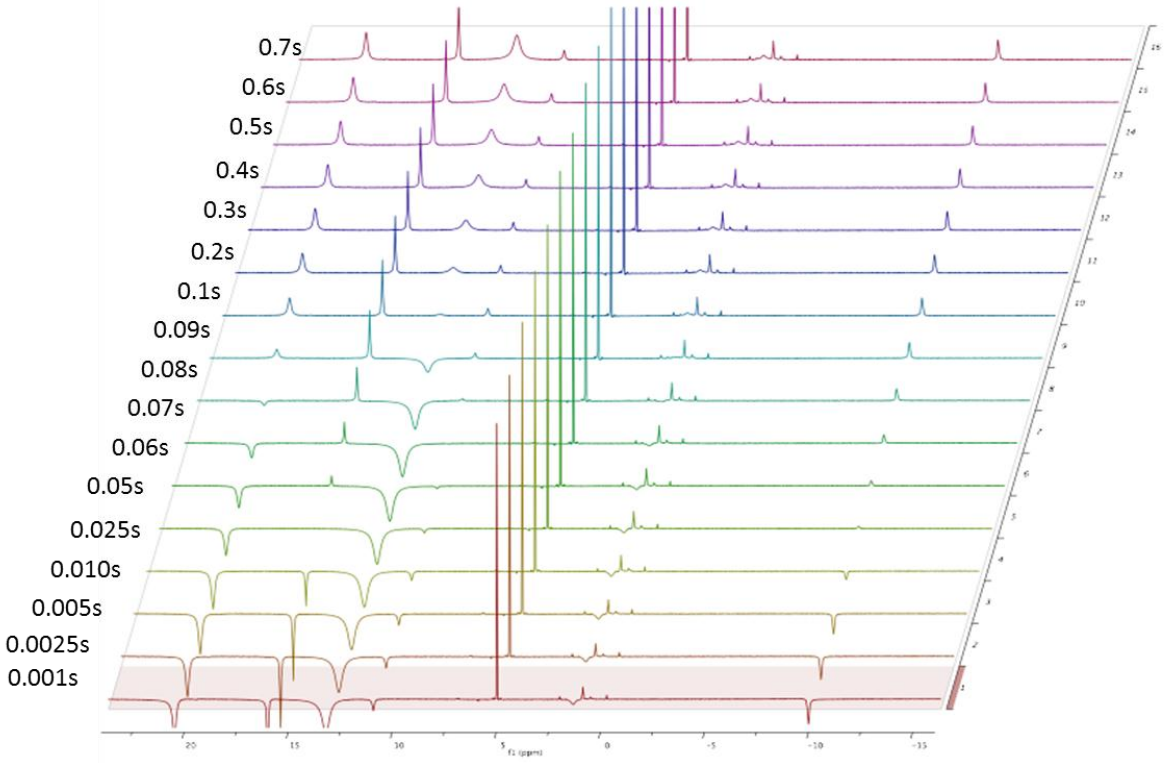
Bis[1-(2,6-dimethylphenylimino)ethyl]pyridine (217 mg, 0.59 mmol) and $ZnBr_2$ (132 mg, 0.59 mmol) were combined with a magnetic stir bar in a 100 mL round bottom flask. Acetonitrile (45 mL) was added via syringe and the reaction was allowed to proceed under nitrogen for 18 hours with stirring. Solvent was removed from the resulting yellow solution by rotary evaporation. The isolated yellow product was heated in a mixture of 2:1 acetonitrile:dichloromethane until dissolved. The yellow solution was removed from heat, allowed to cool to room temperature, and then stored in a freezer for 2 days. The resulting yellow crystals were isolated by vacuum filtration and dried on a Schlenk line. Yield: 286 mg (81.5%) ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.50 (m, 1H), 8.31 (d, J = 7.8 Hz, 2H), 7.16 – 7.03 (m, 6H), 2.33 (s, 6H), 2.23 (s, 12H). ^{13}C NMR (126 MHz, CD_2CL_4) δ 164.04 (s), 148.21 (s), 144.50 (s), 143.52 (s), 128.12 (s), 127.99 (s), 126.39 (s), 125.46 (s), 19.45 (s), 17.18 (s). Calcd for C25H27Br2N3Zn (%): C, 50.49; H, 4.58; N, 7.07.

Found (%): C, 50.22; H, 4.54; N, 7.34. HR FT-ICR MS: Found (calcd for $C_{25}H_{27}Br_2N_3Zn$): *m/z* = $(M\text{-}Br)^+$ 514.0594 (514.0659).

S3: T1 experiment stacked spectra

CD_2Cl_2 T1 data collected on a 500MHz Bruker instrument at -40°C. Data worked up using the Bruker Topspin T1/T2 relaxation module and MestReNova 5.2.4-3824.

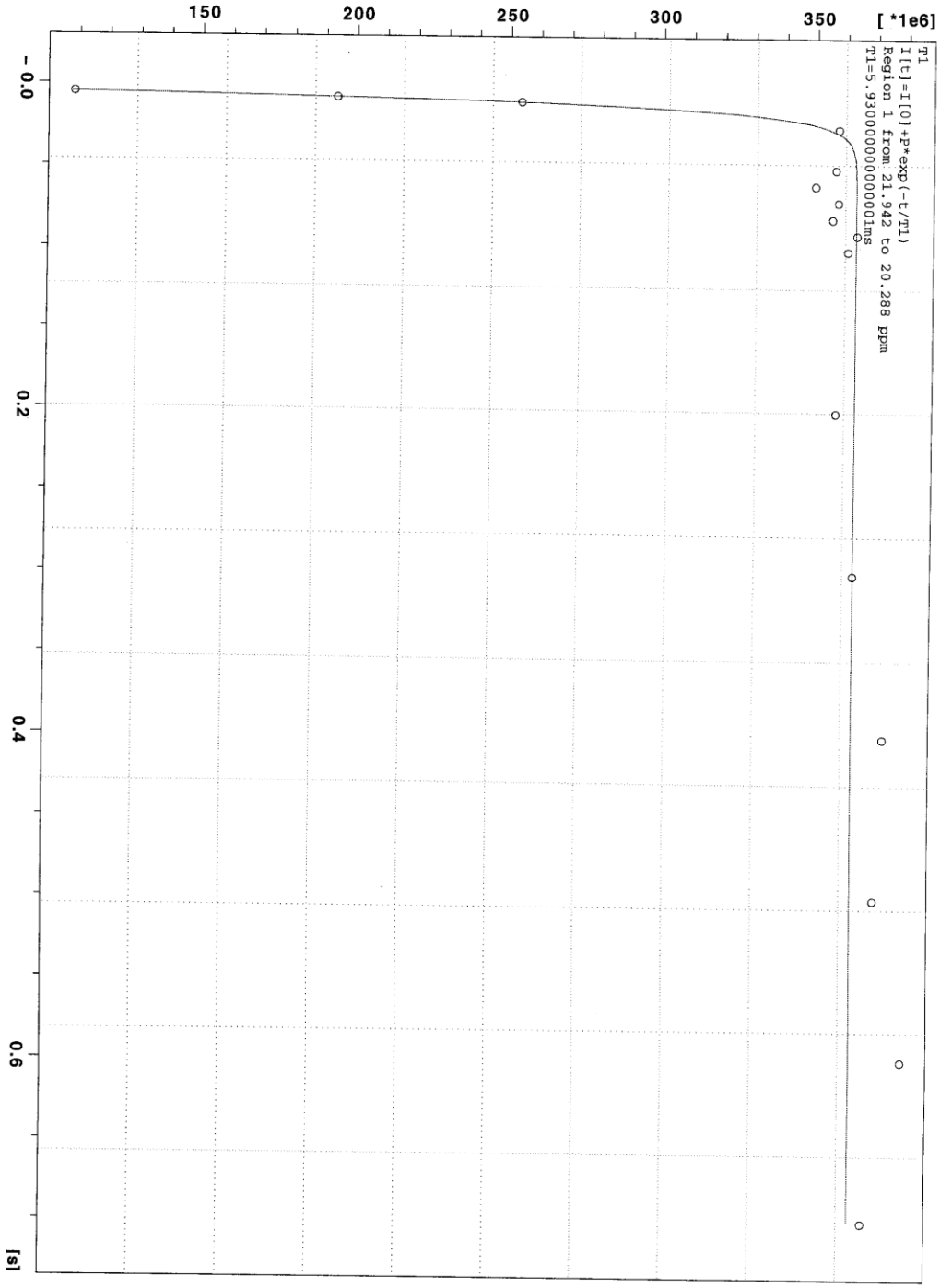
d1=2s, SW=50, 64 scans per datapoint.
Delays: 0.7s, 0.6s, 0.5s, 0.4s, 0.3s, 0.2s, 0.1s, 0.09s, 0.08s, 0.07s, 0.06s, 0.05s, 0.025s, 0.010s, 0.005s, 0.0025s,0.001 Stacked spectra below.

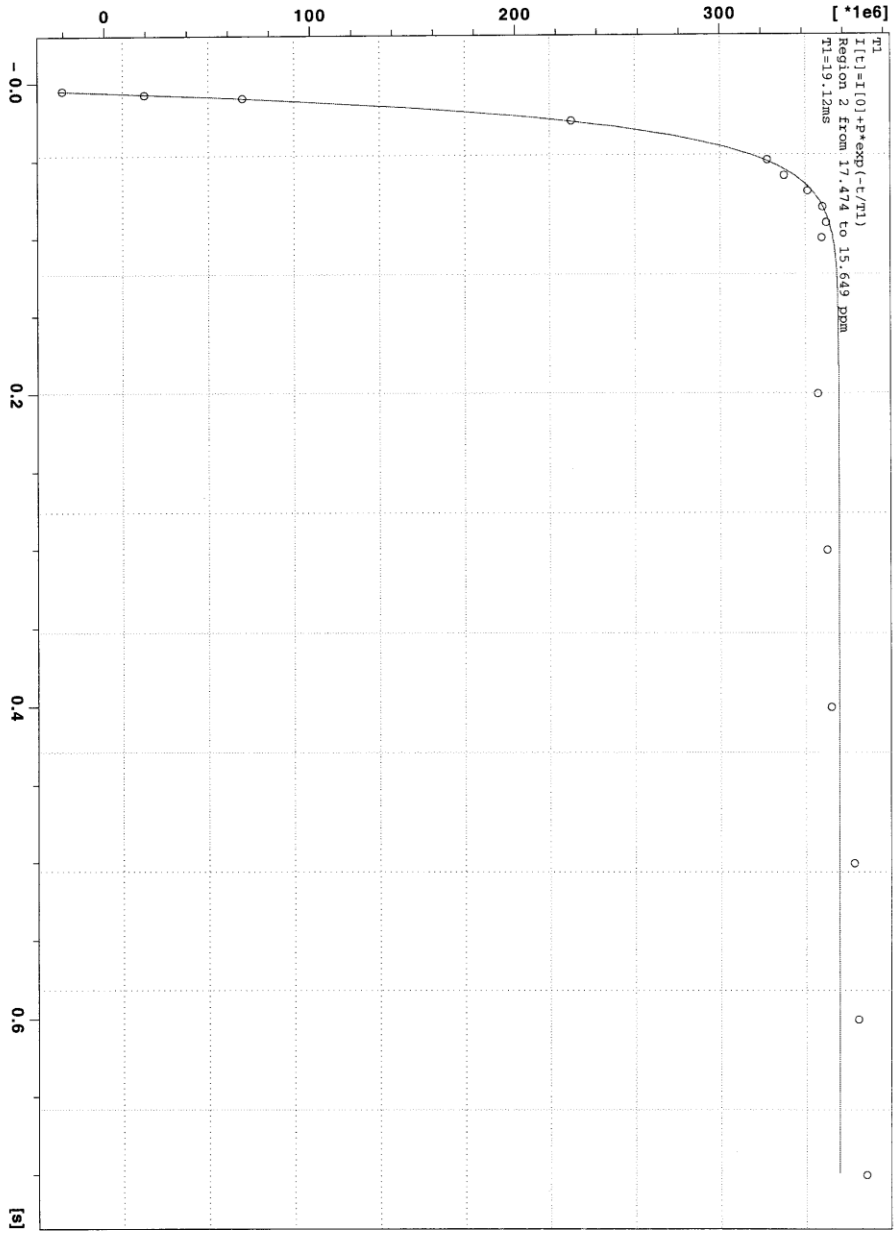


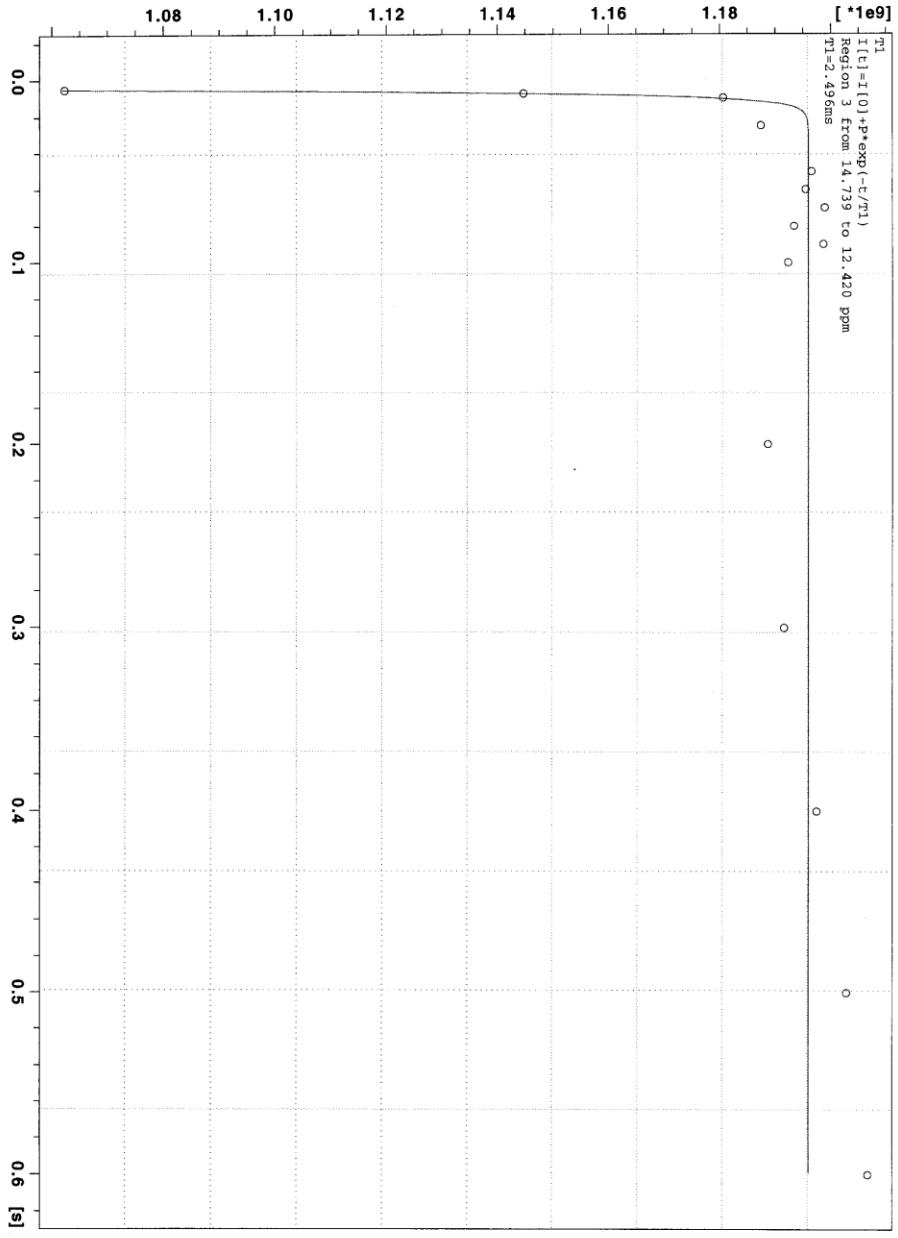
S4: T1 experiment exponential fits

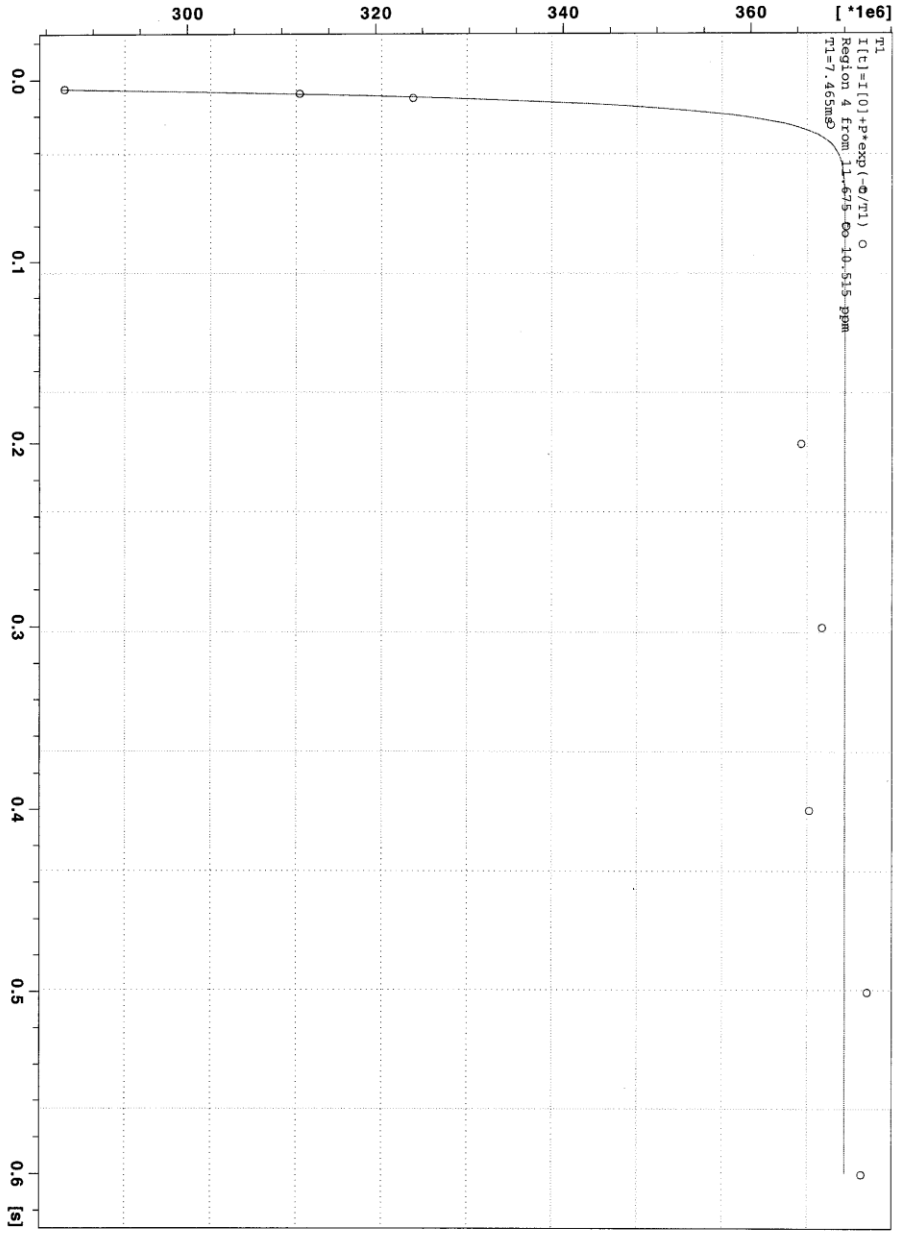
	T1(ms)	r(Å)	r^6(Å^6)
Ha	115	6.44	71337.06
Hb	5.9	4.92	14183.74
Hc	7.4	5.4	24794.91
Hd	2.5	4.3	6321.363
He	19.12	5.88	41329.86
Hf	34	6.63	84933.92

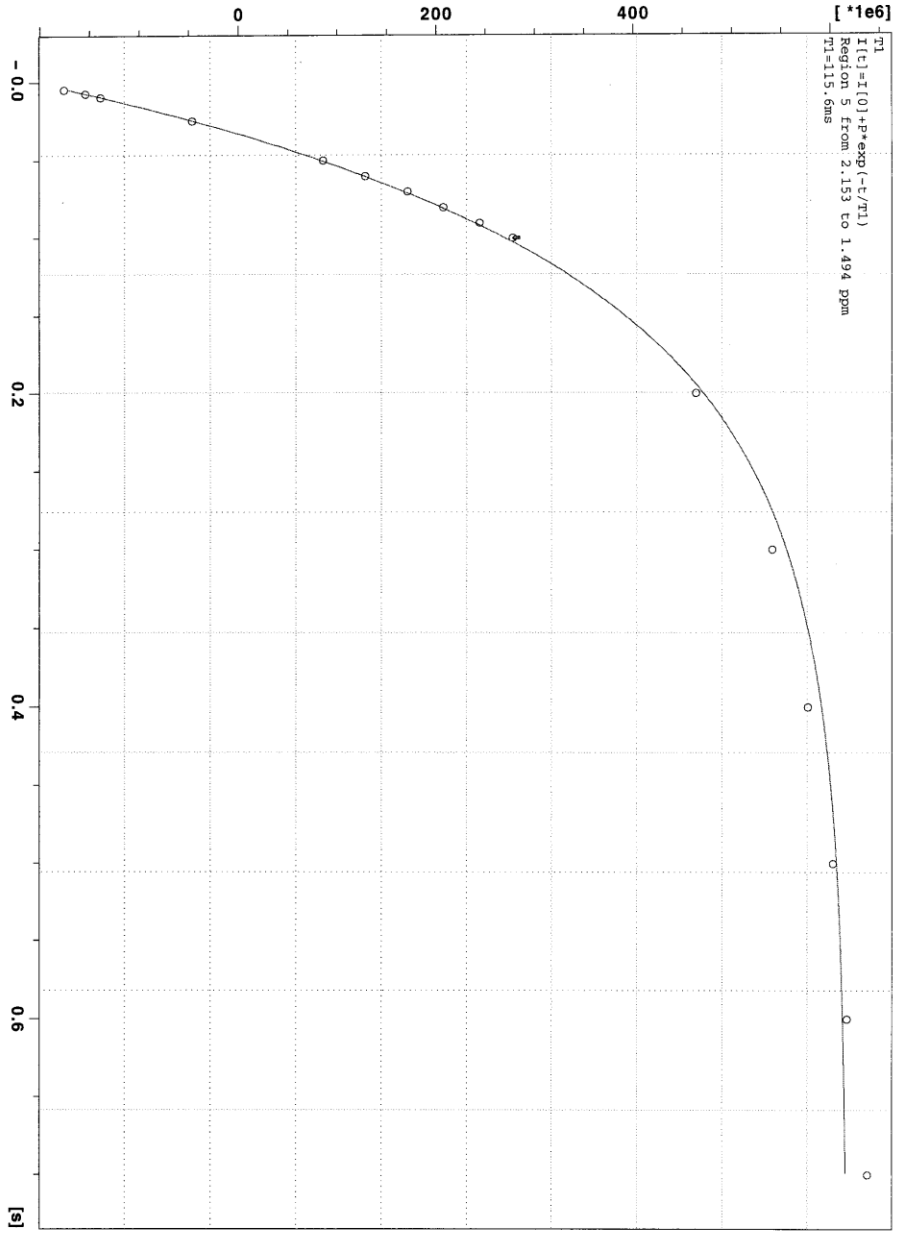
Table S4. Input data for Figure 3 plot. r: average distances between H_x and Ni center from the XRay structure[3], T1: relaxation time determined by exponential fits at 16 delay timepoints.

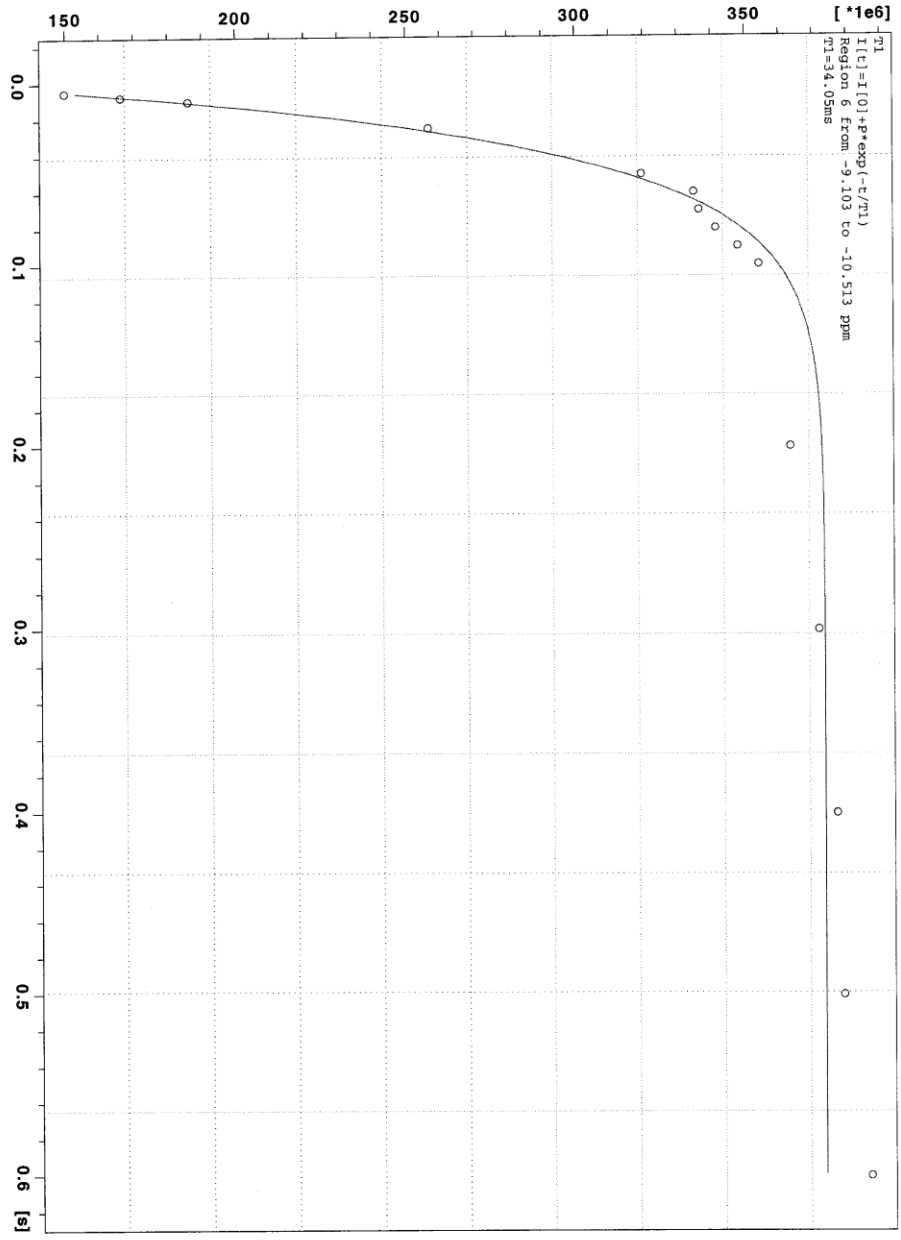



0
100
200
300
[*1e6]
0.0
0.2
0.4
0.6
[s]
T1
I[t]=I[0]+P*exp(-t/T1)
Region 2 from 17.474 to 15.649 ppm
T1=19.12ms


1.08
1.10
1.12
1.14
1.16
1.18
[*1e9]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[s]
T1
I(t)=I(0)+P*exp(-t/T1)
Region 3 from 14.739 to 12.420 ppm
T1=2.496ms


300
320
340
360
[*1e6]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[s]
T1
I(t)=I[0]+P*exp(-t/T1)
Region 4 from 11.675 to 10.515 ppm
T1=7.465ms


0
200
400
[*1e6]
0.0
0.2
0.4
0.6
[s]
T1
I[t]=I[0]+P*exp(-t/T1)
Region 5 from 2.153 to 1.494 ppm
T1=115.6ms


150
200
250
300
350
[*1e6]
0.0
0.1
0.2
0.3
0.4
0.5
0.6
[s]
T1
I[t]=I[0]+P*exp(-t/T1)
Region 6 from -9.103 to -10.513 ppm
T1=34.05ms

S5: X-ray crystal structure of (NNN)$ZnBr_2$

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu K_α (λ = 1.54178 Å) for the structure of KL01. The structure was solved by direct methods using SHELXS[b] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[c] using established refinement techniques.[d] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Compound ZnNNN crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit along with 0.616(7) acetonitrile and 0.383(7) dichloromethane. The partially occupied acetonitrile and dichloromethane share a site and were refined with the help of similarity restraints on the 1,2- and 1,3- distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratio between the two components of this disorder was refined freely and lead to non-integer numbers for C, H, and N in the empirical formula.

Table S5-1. Crystal data and structure refinement for ZnNNN.

Empirical formula	C26.62 H29.62 Br2 Cl0.77 N3.62 Zn	
Formula weight	652.77	
Temperature	93(2) K	
Wavelength	1.54187 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.0658(2) Å	α= 90°.
	b = 14.9486(3) Å	β= 107.768(8)°.
	c = 14.4262(10) Å	γ = 90°.
Volume	2683.3(2) Å^3	
Z	4	

Density (calculated)	1.616 Mg/m^3
Absorption coefficient	5.625 mm^{-1}
F(000)	1311
Crystal size	0.10 x 0.09 x 0.04 mm^3
Theta range for data collection	6.91 to 65.06°.
Index ranges	-15<=h<=12, -16<=k<=17, -15<=l<=16
Reflections collected	12805
Independent reflections	4435 [R(int) = 0.0717]
Completeness to theta = 65.06°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8063 and 0.6031
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4435 / 48 / 342
Goodness-of-fit on F^2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.1263
R indices (all data)	R1 = 0.0504, wR2 = 0.1291
Largest diff. peak and hole	0.702 and -0.755 $e.Å^{-3}$

Table S5-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for KL01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	7598(1)	3678(1)	5679(1)	28(1)
Br(2)	8067(1)	4469(1)	8442(1)	31(1)
Zn(1)	8220(1)	3310(1)	7367(1)	24(1)
N(1)	8885(3)	2116(2)	7990(2)	24(1)
C(1)	9944(3)	1954(3)	8157(3)	26(1)
C(2)	10389(3)	1134(3)	8516(3)	28(1)
C(3)	9739(4)	484(3)	8737(3)	29(1)
C(4)	8670(4)	672(3)	8596(3)	28(1)
C(5)	8258(3)	1496(3)	8209(3)	26(1)
N(2)	6799(3)	2452(2)	7481(2)	26(1)
C(6)	7097(3)	1732(3)	7975(3)	26(1)
C(7)	6383(4)	1113(3)	8296(3)	34(1)
C(10)	5681(3)	2707(3)	7141(3)	28(1)
C(11)	5215(4)	3186(3)	7745(4)	36(1)
C(17)	5799(4)	3333(4)	8805(4)	50(1)
C(12)	4159(5)	3490(4)	7344(4)	50(1)
C(13)	3575(4)	3297(4)	6393(4)	48(1)
C(14)	4037(4)	2784(4)	5831(4)	42(1)
C(15)	5091(3)	2475(3)	6180(3)	30(1)
C(16)	5571(4)	1895(3)	5572(3)	34(1)
C(8)	10571(3)	2702(3)	7901(3)	25(1)
C(9)	11748(3)	2566(3)	8081(3)	33(1)
N(3)	10044(3)	3406(2)	7545(2)	23(1)
C(18)	10588(3)	4142(3)	7248(3)	26(1)
C(19)	10997(3)	4843(3)	7896(3)	28(1)
C(25)	10992(4)	4811(3)	8935(3)	37(1)
C(20)	11443(4)	5574(3)	7551(3)	33(1)
C(21)	11482(4)	5595(3)	6608(3)	34(1)
C(22)	11117(3)	4881(3)	5998(3)	32(1)
C(23)	10682(3)	4133(3)	6307(3)	28(1)
C(24)	10347(4)	3332(3)	5649(3)	30(1)

N(1S)	4300(20)	5799(15)	8860(20)	51(6)
C(1S)	5201(8)	5901(6)	9101(6)	43(2)
C(2S)	6347(9)	5996(13)	9493(11)	70(3)
C(1T)	5795(12)	5467(10)	9127(11)	40(3)
Cl(1T)	4362(10)	5578(7)	8766(10)	40(2)
Cl(2T)	6444(3)	6503(3)	9366(3)	39(1)

Table S5-3. Bond lengths [Å] and angles [°] for KL01.

Br(1)-Zn(1)	2.3848(7)
Br(2)-Zn(1)	2.3737(7)
Zn(1)-N(1)	2.067(4)
Zn(1)-N(2)	2.303(3)
Zn(1)-N(3)	2.322(3)
N(1)-C(5)	1.338(5)
N(1)-C(1)	1.351(5)
C(1)-C(2)	1.387(6)
C(1)-C(8)	1.499(6)
C(2)-C(3)	1.390(6)
C(2)-H(2)	0.9500
C(3)-C(4)	1.378(6)
C(3)-H(3)	0.9500
C(4)-C(5)	1.390(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.492(6)
N(2)-C(6)	1.284(6)
N(2)-C(10)	1.443(5)
C(6)-C(7)	1.485(6)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(10)-C(11)	1.403(7)
C(10)-C(15)	1.408(6)
C(11)-C(12)	1.398(7)
C(11)-C(17)	1.503(7)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(12)-C(13)	1.381(8)
C(12)-H(12)	0.9500
C(13)-C(14)	1.382(8)
C(13)-H(13)	0.9500
C(14)-C(15)	1.393(7)

C(14)-H(14)	0.9500
C(15)-C(16)	1.500(7)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(8)-N(3)	1.277(5)
C(8)-C(9)	1.493(6)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
N(3)-C(18)	1.444(5)
C(18)-C(19)	1.396(6)
C(18)-C(23)	1.401(6)
C(19)-C(20)	1.400(6)
C(19)-C(25)	1.502(6)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(20)-C(21)	1.377(7)
C(20)-H(20)	0.9500
C(21)-C(22)	1.375(7)
C(21)-H(21)	0.9500
C(22)-C(23)	1.388(6)
C(22)-H(22)	0.9500
C(23)-C(24)	1.507(6)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
N(1S)-C(1S)	1.13(3)
C(1S)-C(2S)	1.437(15)
C(2S)-H(2S1)	0.9800
C(2S)-H(2S2)	0.9800
C(2S)-H(2S3)	0.9800
C(1T)-Cl(2T)	1.749(14)
C(1T)-Cl(1T)	1.791(19)
C(1T)-H(1T1)	0.9900

C(1T)-H(1T2)	0.9900
N(1)-Zn(1)-N(2)	74.28(13)
N(1)-Zn(1)-N(3)	73.99(13)
N(2)-Zn(1)-N(3)	148.08(13)
N(1)-Zn(1)-Br(2)	116.99(9)
N(2)-Zn(1)-Br(2)	97.45(9)
N(3)-Zn(1)-Br(2)	99.83(9)
N(1)-Zn(1)-Br(1)	127.61(9)
N(2)-Zn(1)-Br(1)	99.81(8)
N(3)-Zn(1)-Br(1)	96.72(8)
Br(2)-Zn(1)-Br(1)	115.39(3)
C(5)-N(1)-C(1)	120.1(4)
C(5)-N(1)-Zn(1)	119.6(3)
C(1)-N(1)-Zn(1)	120.3(3)
N(1)-C(1)-C(2)	121.0(4)
N(1)-C(1)-C(8)	115.4(4)
C(2)-C(1)-C(8)	123.5(4)
C(1)-C(2)-C(3)	119.1(4)
C(1)-C(2)-H(2)	120.4
C(3)-C(2)-H(2)	120.4
C(4)-C(3)-C(2)	119.1(4)
C(4)-C(3)-H(3)	120.5
C(2)-C(3)-H(3)	120.5
C(3)-C(4)-C(5)	119.4(4)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
N(1)-C(5)-C(4)	121.2(4)
N(1)-C(5)-C(6)	115.9(4)
C(4)-C(5)-C(6)	122.8(4)
C(6)-N(2)-C(10)	120.9(4)
C(6)-N(2)-Zn(1)	113.1(3)
C(10)-N(2)-Zn(1)	125.7(3)
N(2)-C(6)-C(7)	125.7(4)
N(2)-C(6)-C(5)	116.0(4)
C(7)-C(6)-C(5)	118.3(4)

C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(11)-C(10)-C(15)	121.7(4)
C(11)-C(10)-N(2)	120.7(4)
C(15)-C(10)-N(2)	117.6(4)
C(12)-C(11)-C(10)	117.9(5)
C(12)-C(11)-C(17)	120.3(5)
C(10)-C(11)-C(17)	121.6(4)
C(11)-C(17)-H(17A)	109.5
C(11)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(11)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(13)-C(12)-C(11)	121.4(5)
C(13)-C(12)-H(12)	119.3
C(11)-C(12)-H(12)	119.3
C(12)-C(13)-C(14)	119.3(5)
C(12)-C(13)-H(13)	120.3
C(14)-C(13)-H(13)	120.3
C(13)-C(14)-C(15)	122.2(5)
C(13)-C(14)-H(14)	118.9
C(15)-C(14)-H(14)	118.9
C(14)-C(15)-C(10)	117.3(4)
C(14)-C(15)-C(16)	121.6(4)
C(10)-C(15)-C(16)	121.1(4)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

N(3)-C(8)-C(9)	125.7(4)
N(3)-C(8)-C(1)	116.5(4)
C(9)-C(8)-C(1)	117.9(4)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-N(3)-C(18)	119.5(3)
C(8)-N(3)-Zn(1)	113.8(3)
C(18)-N(3)-Zn(1)	126.6(3)
C(19)-C(18)-C(23)	121.8(4)
C(19)-C(18)-N(3)	119.7(4)
C(23)-C(18)-N(3)	118.5(4)
C(18)-C(19)-C(20)	117.7(4)
C(18)-C(19)-C(25)	121.8(4)
C(20)-C(19)-C(25)	120.5(4)
C(19)-C(25)-H(25A)	109.5
C(19)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(19)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(21)-C(20)-C(19)	120.9(4)
C(21)-C(20)-H(20)	119.6
C(19)-C(20)-H(20)	119.6
C(22)-C(21)-C(20)	120.4(4)
C(22)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	121.1(4)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(22)-C(23)-C(18)	118.0(4)
C(22)-C(23)-C(24)	120.4(4)
C(18)-C(23)-C(24)	121.6(4)

C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(1S)-C(1S)-C(2S)	175.0(19)
Cl(2T)-C(1T)-Cl(1T)	112.1(9)
Cl(2T)-C(1T)-H(1T1)	109.2
Cl(1T)-C(1T)-H(1T1)	109.2
Cl(2T)-C(1T)-H(1T2)	109.2
Cl(1T)-C(1T)-H(1T2)	109.2
H(1T1)-C(1T)-H(1T2)	107.9

Symmetry transformations used to generate equivalent atoms:

Table S-5-4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for KL01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	26(1)	34(1)	19(1)	1(1)	1(1)	1(1)
Br(2)	30(1)	36(1)	26(1)	-6(1)	4(1)	3(1)
Zn(1)	23(1)	28(1)	19(1)	1(1)	2(1)	1(1)
N(1)	20(2)	31(2)	19(2)	1(1)	3(1)	-3(2)
C(1)	23(2)	33(2)	18(2)	3(2)	0(2)	2(2)
C(2)	24(2)	34(2)	20(2)	0(2)	-1(2)	2(2)
C(3)	32(2)	29(2)	21(2)	2(2)	-1(2)	-2(2)
C(4)	26(2)	31(2)	23(2)	1(2)	3(2)	-2(2)
C(5)	25(2)	31(2)	19(2)	-1(2)	3(2)	-1(2)
N(2)	20(2)	30(2)	23(2)	-3(1)	2(1)	-3(1)
C(6)	27(2)	29(2)	20(2)	-6(2)	4(2)	-7(2)
C(7)	27(2)	35(3)	39(3)	6(2)	9(2)	-3(2)
C(10)	16(2)	32(2)	35(2)	2(2)	8(2)	0(2)
C(11)	26(2)	42(3)	43(3)	-2(2)	15(2)	-5(2)
C(17)	39(3)	70(4)	46(3)	-10(3)	23(2)	-3(3)
C(12)	43(3)	50(3)	65(4)	1(3)	29(3)	5(3)
C(13)	18(2)	60(4)	63(4)	13(3)	11(2)	6(2)
C(14)	28(3)	50(3)	44(3)	16(2)	5(2)	1(2)
C(15)	19(2)	37(3)	30(2)	7(2)	0(2)	0(2)
C(16)	29(2)	37(3)	27(2)	-1(2)	-3(2)	-5(2)
C(8)	22(2)	32(2)	20(2)	1(2)	4(2)	2(2)
C(9)	27(2)	37(3)	33(2)	8(2)	5(2)	5(2)
N(3)	17(2)	32(2)	19(2)	1(1)	2(1)	-1(1)
C(18)	15(2)	32(2)	29(2)	6(2)	4(2)	1(2)
C(19)	18(2)	31(2)	29(2)	2(2)	-2(2)	1(2)
C(25)	31(3)	45(3)	30(2)	-4(2)	3(2)	-4(2)
C(20)	21(2)	34(2)	37(3)	2(2)	0(2)	-4(2)
C(21)	22(2)	37(3)	39(3)	8(2)	6(2)	-6(2)
C(22)	21(2)	44(3)	30(2)	6(2)	7(2)	2(2)
C(23)	16(2)	36(2)	28(2)	6(2)	3(2)	3(2)
C(24)	32(2)	35(3)	26(2)	2(2)	11(2)	-1(2)

N(1S)	47(5)	68(14)	28(6)	-23(8)	-3(5)	-5(8)
C(1S)	45(4)	47(5)	33(4)	-8(4)	4(4)	4(4)
C(2S)	41(4)	65(9)	93(9)	-20(8)	5(5)	5(6)
C(1T)	35(5)	34(6)	50(7)	1(6)	13(6)	0(5)
Cl(1T)	35(2)	48(4)	41(4)	-10(3)	15(2)	-3(2)
Cl(2T)	33(2)	38(3)	40(2)	0(2)	4(1)	0(2)

Table S5-6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for KL01.

	x	y	z	U(eq)
H(2)	11129	1019	8609	33
H(3)	10028	-82	8982	35
H(4)	8218	243	8761	33
H(7A)	5670	1384	8167	51
H(7B)	6688	998	8995	51
H(7C)	6319	548	7938	51
H(17A)	5902	2758	9147	74
H(17B)	5376	3731	9086	74
H(17C)	6501	3605	8874	74
H(12)	3838	3836	7733	60
H(13)	2861	3514	6129	57
H(14)	3623	2638	5184	50
H(16A)	5030	1774	4946	50
H(16B)	5812	1330	5912	50
H(16C)	6186	2203	5462	50
H(9A)	12074	3126	7956	50
H(9B)	11860	2099	7646	50
H(9C)	12083	2385	8759	50
H(25A)	11321	5358	9271	55
H(25B)	11401	4290	9259	55
H(25C)	10249	4766	8952	55
H(20)	11723	6063	7974	39
H(21)	11762	6107	6379	40
H(22)	11163	4899	5353	38
H(24A)	10319	3497	4985	46
H(24B)	9636	3130	5655	46
H(24C)	10870	2848	5881	46
H(2S1)	6584	5773	10164	105
H(2S2)	6541	6628	9485	105
H(2S3)	6696	5650	9097	105

H(1T1)	6033	5089	9718	48
H(1T2)	6004	5162	8603	48

S6: Computational data and full Gaussian09 reference

S6-T1. Atomic coordinates of NiNNN obtained at the DFT UB3LYP/LANL2DZ/6-311++G(d,p) level. Structure is shown in Figure 1 of the main text.

Br	-9.2E-05	-2.47002	0.08858
Br	-0.00016	0.71534	2.50375
Ni	-0.00038	-0.01307	0.073778
N	-0.00018	1.902111	-0.5808
N	2.15538	0.426582	-0.31788
N	-2.1557	0.427114	-0.31669
C	1.167872	2.536029	-0.71275
C	1.204898	3.908278	-0.96628
C	-0.00002	4.595822	-1.08179
C	-1.20504	3.908613	-0.96535
C	-1.16817	2.53637	-0.71187
C	2.374745	1.658497	-0.60953
C	3.716701	2.267086	-0.89097
C	-2.37512	1.659056	-0.60811
C	-3.71718	2.267663	-0.88896
C	3.22663	-0.52796	-0.28023
C	3.434243	-1.32455	-1.42157
C	4.44086	-2.29201	-1.37744
C	5.214265	-2.47183	-0.2343
C	4.993313	-1.67004	0.880456
C	4.003503	-0.68117	0.881217
C	2.608354	-1.13436	-2.66889
C	3.812489	0.198953	2.090975
C	-3.22664	-0.52778	-0.27992
C	-3.43357	-1.32308	-1.42223
C	-4.43922	-2.29158	-1.37939
C	-5.21254	-2.47338	-0.2365
C	-4.9924	-1.67269	0.879219
C	-4.0034	-0.68298	0.881288
C	-2.60804	-1.12963	-2.66924
C	-3.81309	0.195922	2.09203
H	2.145076	4.431248	-1.07068
H	0.00005	5.661963	-1.27102

H	-2.14517	4.431815	-1.06904
H	4.502613	1.515889	-0.88071
H	3.711523	2.761946	-1.86558
H	3.9484	3.02812	-0.13974
H	-3.94843	3.028866	-0.13777
H	-3.71256	2.762293	-1.86369
H	-4.50313	1.516508	-0.87808
H	4.611539	-2.9119	-2.25109
H	5.984853	-3.23417	-0.21253
H	5.596531	-1.80469	1.771972
H	1.545696	-1.28429	-2.46051
H	2.723337	-0.12806	-3.08396
H	2.907164	-1.84845	-3.43768
H	4.194522	1.210316	1.911675
H	2.760068	0.294658	2.362781
H	4.356984	-0.20712	2.945049
H	-4.60911	-2.91073	-2.25373
H	-5.98236	-3.23653	-0.21563
H	-5.59552	-1.80899	1.770548
H	-2.73314	-0.12616	-3.08843
H	-1.54419	-1.26725	-2.4589
H	-2.89841	-1.84977	-3.4356
H	-2.76068	0.292844	2.363437
H	-4.19664	1.206948	1.914024
H	-4.35663	-0.21192	2.94587

The full Gaussian09 refernce is given below:

Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

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