Supplementary Material

CCC-NHC pincer Zr diamido complexes: Synthesis, characterization, and catalytic activity in hydroamination/cyclization of unactivated amino-alkenes, -alkynes, and allenes

Henry U. Valle,[a] Gopalkrishna Akurathi,[a] Joon Cho[b], Wesley D. Clark[a], Amarraj Chakraborty,[a]
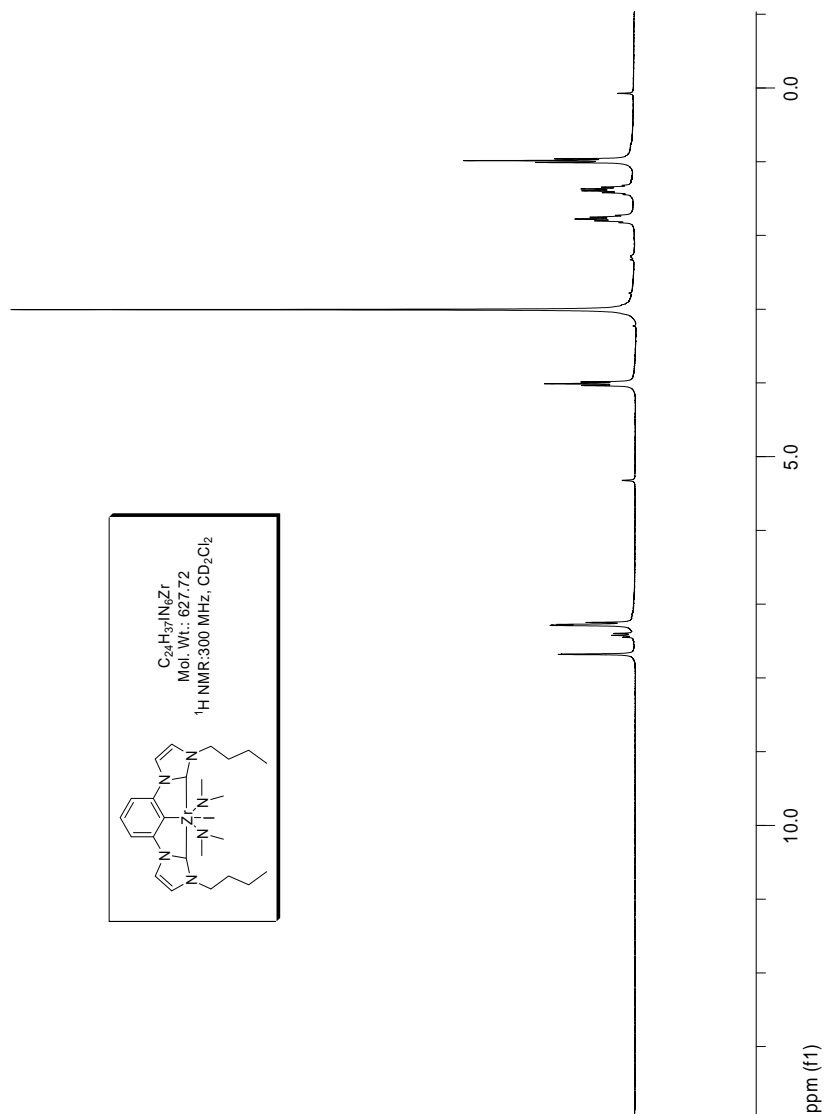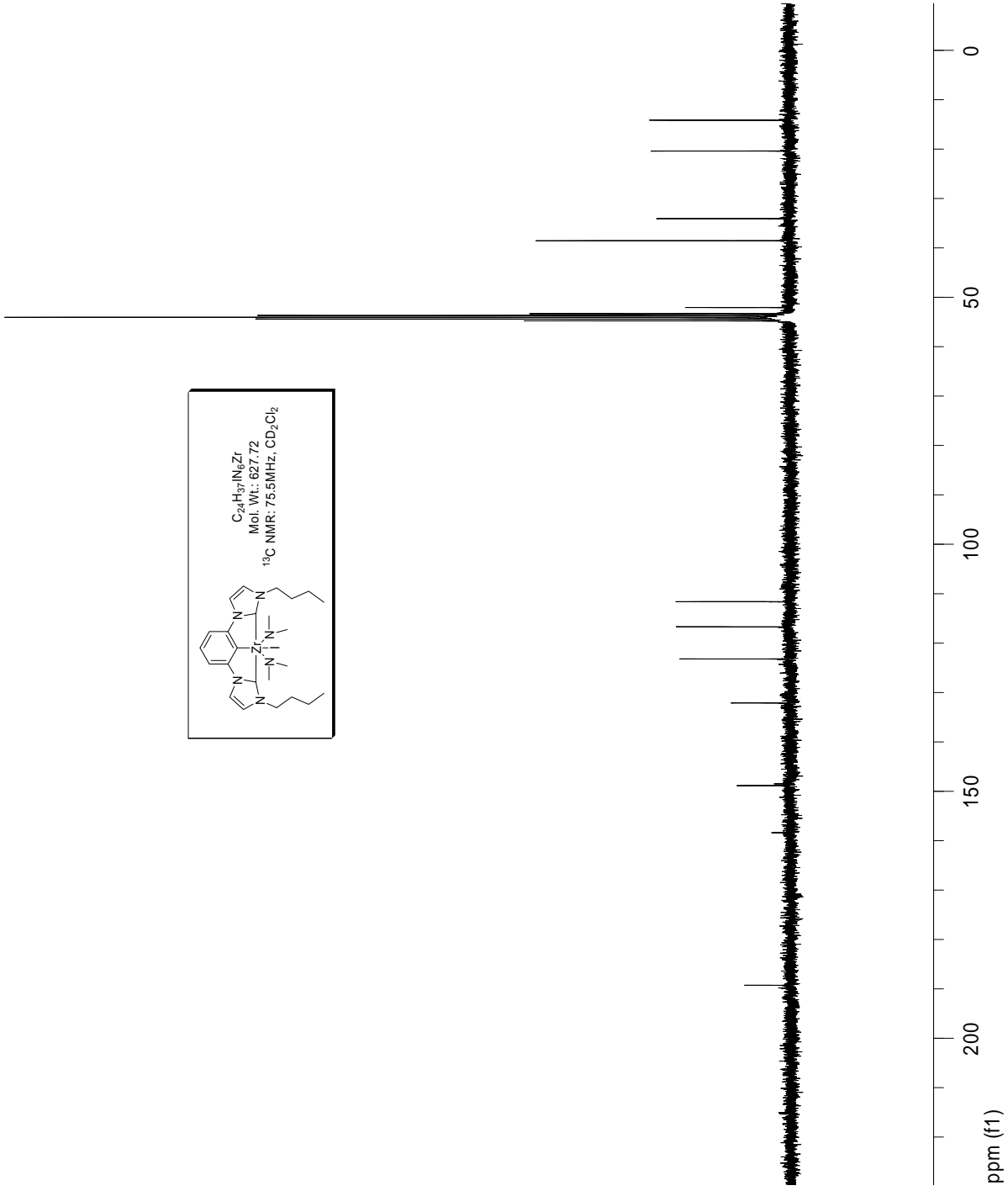
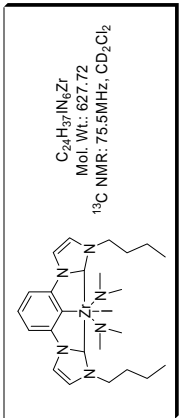*T. Keith Hollis*[a,b]*

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NMR spectroscopic data

C$_{24}$H$_{37}$IN$_6$Zr
Mol. Wt.: 627.72
^{1}H NMR:300 MHz, CD$_2$Cl$_2$

ppm (f1)

0.0

5.0

10.0

$C_{24}H_{37}IN_6Zr$
Mol. Wt.: 627.72
^{13}C NMR: 75.5MHz, CD_2Cl_2

ppm (f1)

Complex **4** - toluene preparation

C$_{24}$H$_{37}$BrN$_6$Zr
Mol. Wt.: 580.72
^{1}H NMR:500 MHz, CD$_2$Cl$_2$

10.0   5.0   0.0

ppm (f1)

Complex **4** - toluene preparation

$C_{24}H_{37}BrN_6Zr$
Mol. Wt.: 580.72
^{13}C NMR: 125 MHz, CD_2Cl_2

ppm (f1)

THFprparat.m

BRUKER

* = trace NMe₂H
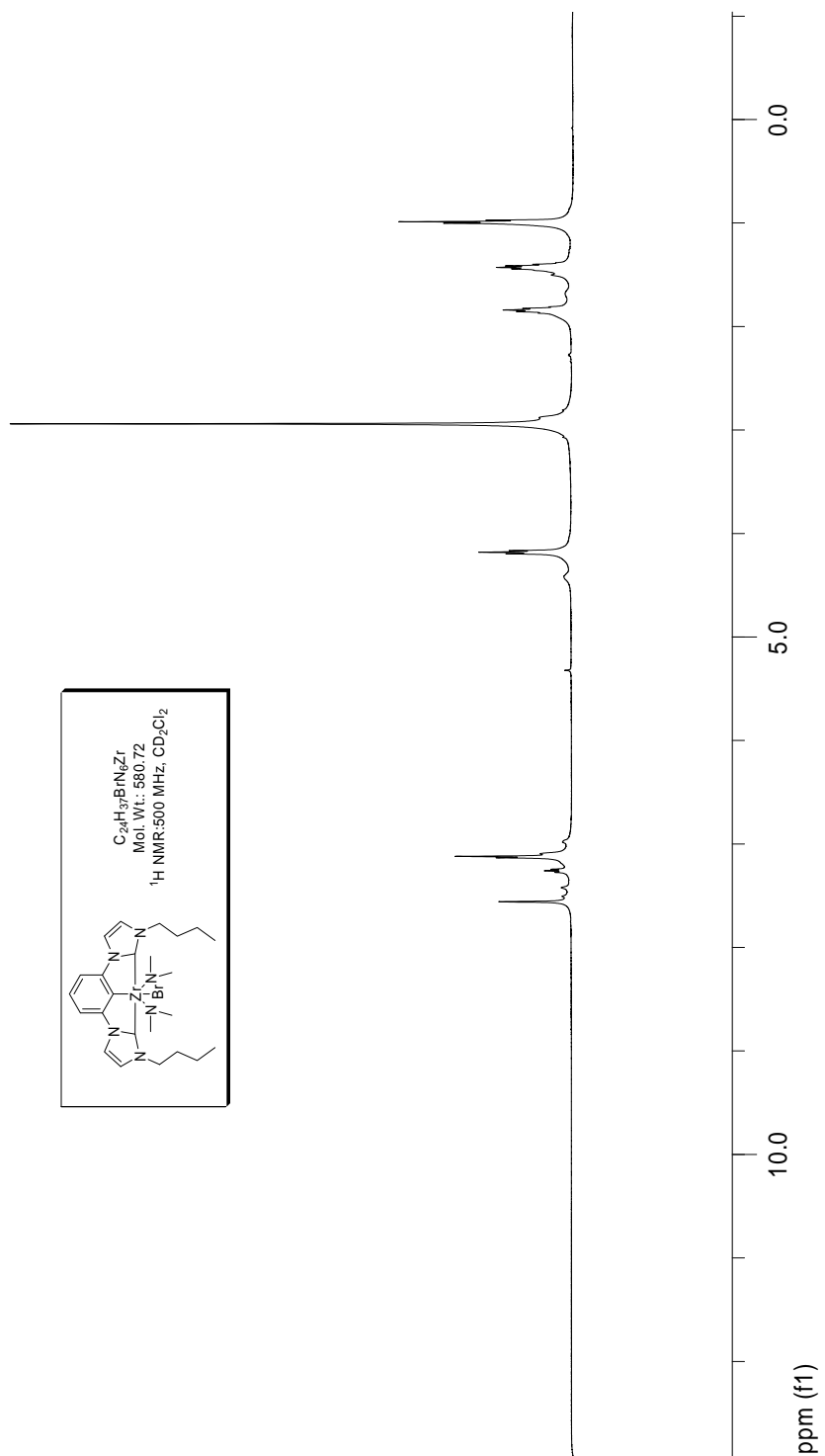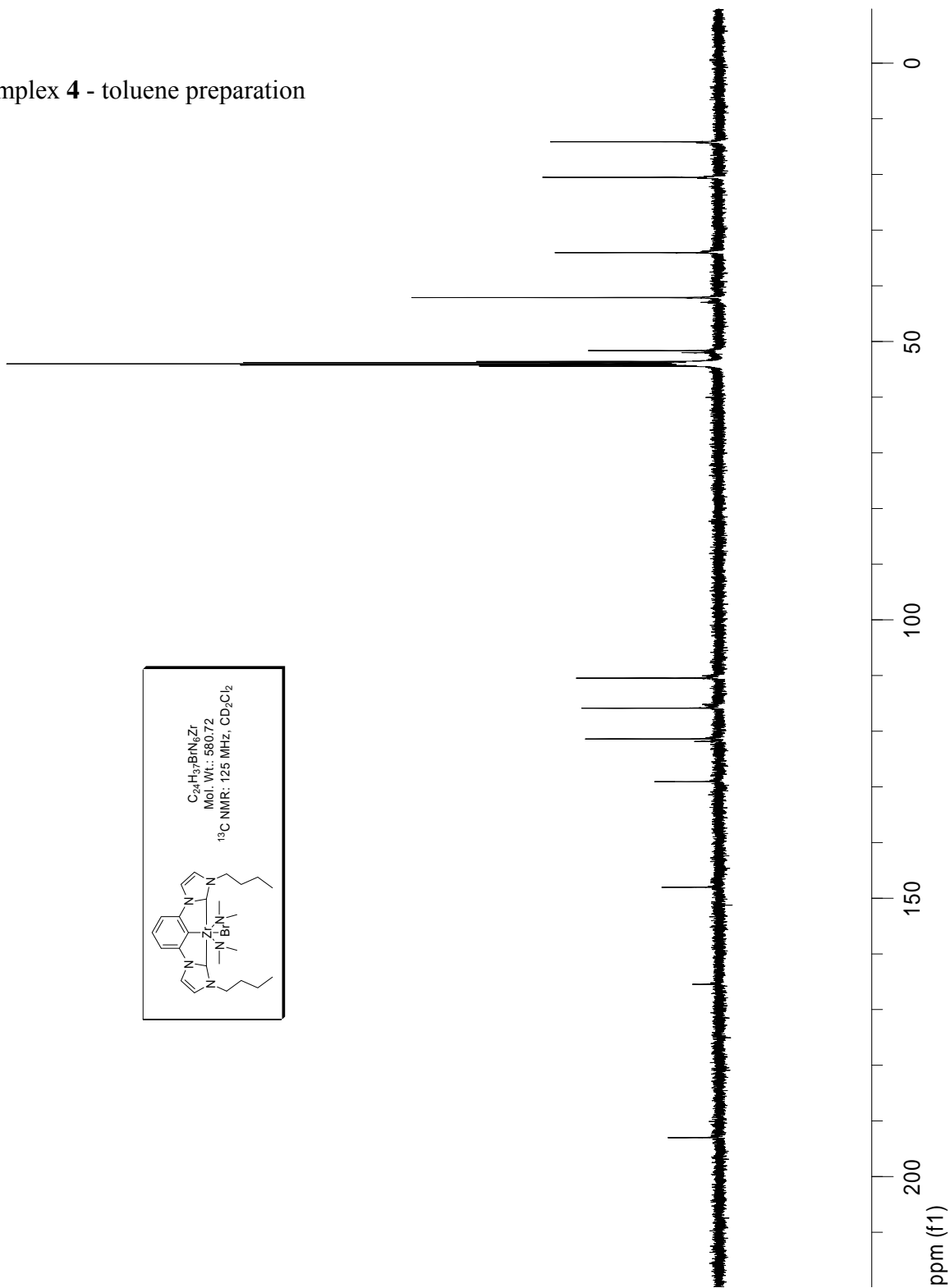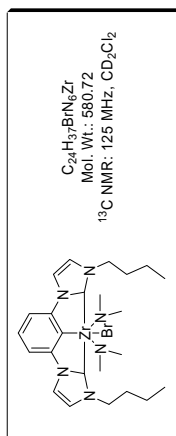
WDC-2-168-3-proton
After drying overnight
Expno 2
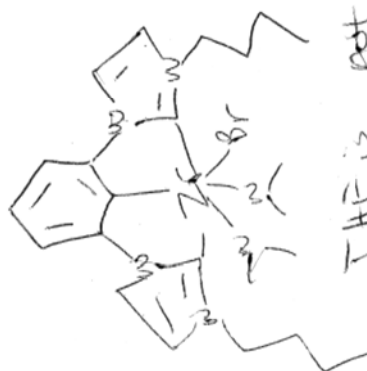
THF is not
present after
drying at 70°C
under High vac.

Sample still looks
crystalline & no though.

Table 2 entry 1

5-Methyl-3,3-diphenyl-3,4-dihydro-2*H*-pyrrole:
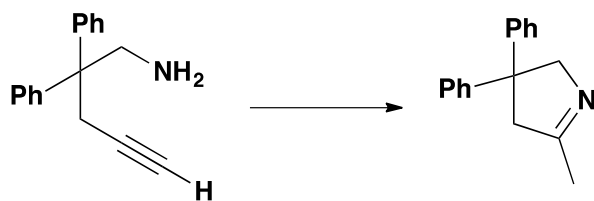
In a screw cap NMR tube 2,2-diphenyl-4-pentyn-1-amine (0.025 g, 0.106 mmol), 2-(1,3-Bis(N-butyl-imidazol-2ylidene) phenylene)bis(dimethylamido)(iodo)zirconium (IV) (0.004 g, 0.0054 mmol) and 0.4 ml of tol-d$_8$ was added in glove box and heated the reaction mixture at 160 °C. The progress of the reaction was monitored by using ^{1}H NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 300MHz): δ 7.08-6.95 (m, 10H), 4.38-4.36 (q, J= 1.5 Hz, 2H), 2.68 (s, 2H), 1.75-1.74 (t, J = 1.8 Hz, 3H).

The proton NMR of this compound showed coupling not reported previously in the literature. The spectrum is included here for reference.

Standard 1H

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

10.22   2.00   1.99   2.92

4.40 ppm   7.081
2.00   7.077
              7.071
              7.057
              7.052
              7.050
              7.040
              7.029
              7.027
              7.000
              6.997
              6.983
              6.975
              6.965
              6.959
              6.954

              4.379
              4.374
              4.369
              4.363

2.7 ppm   4.379
1.99   4.374
              4.369
              4.363

              2.686

1.76 ppm   2.686
2.92   2.206
              2.185
              2.095
              2.088
              2.080
              2.073
              2.066
              1.757
              1.751
              1.745

              1.757
              1.751
              1.745
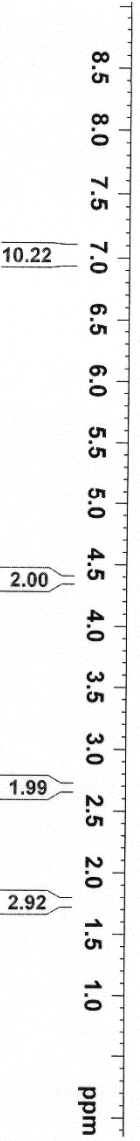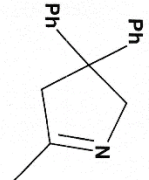
Partial 1H NMR spectrum from Table 1 entry 1 catalytic trial
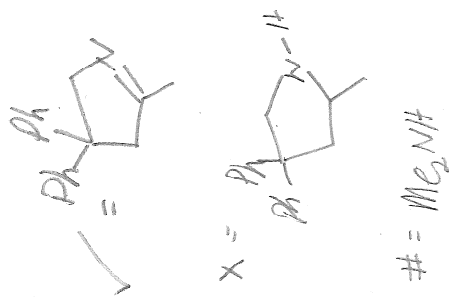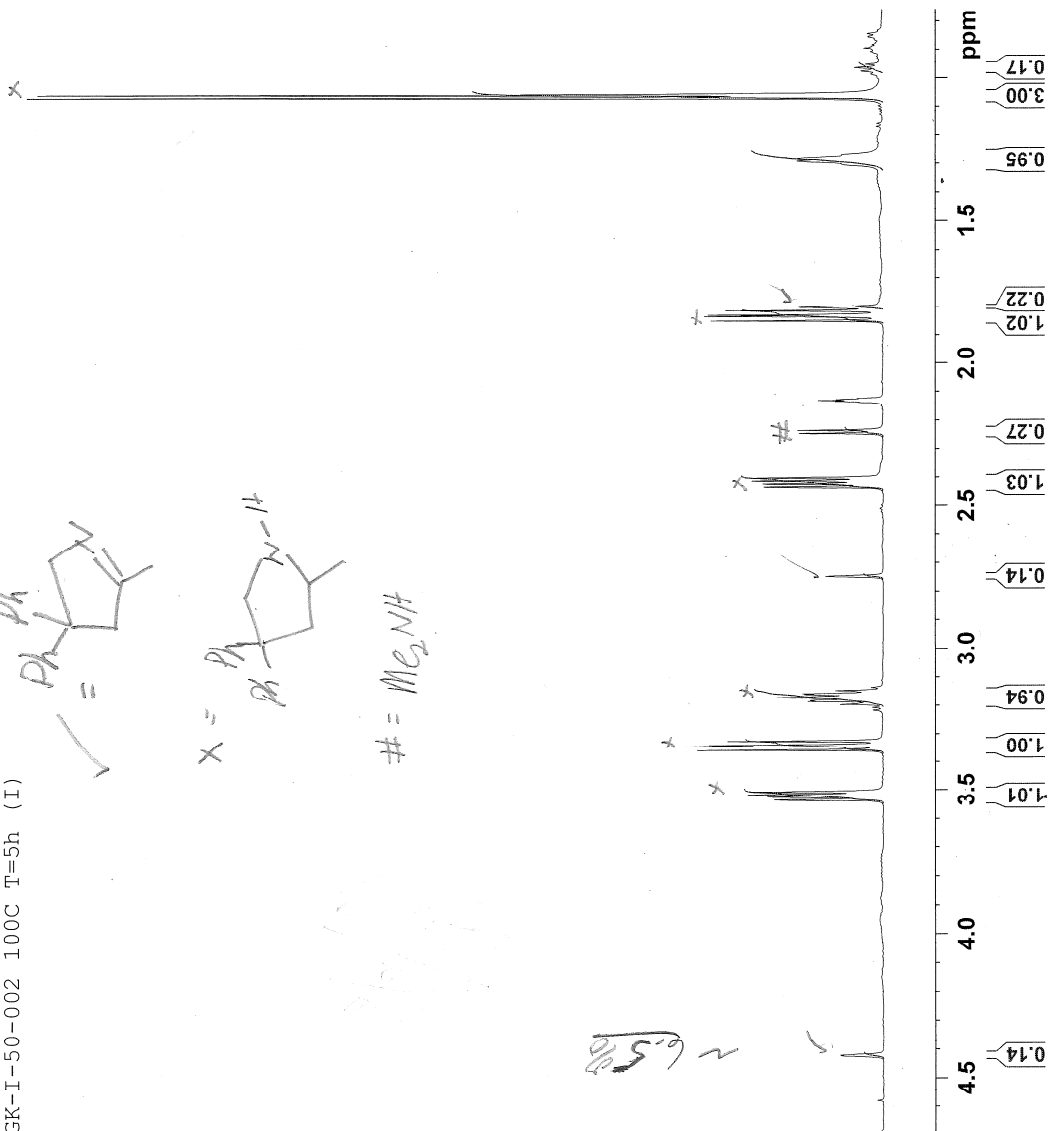
Partial 1H NMR spectrum from Table 1 entry 5 catalytic trial

Standard 1H
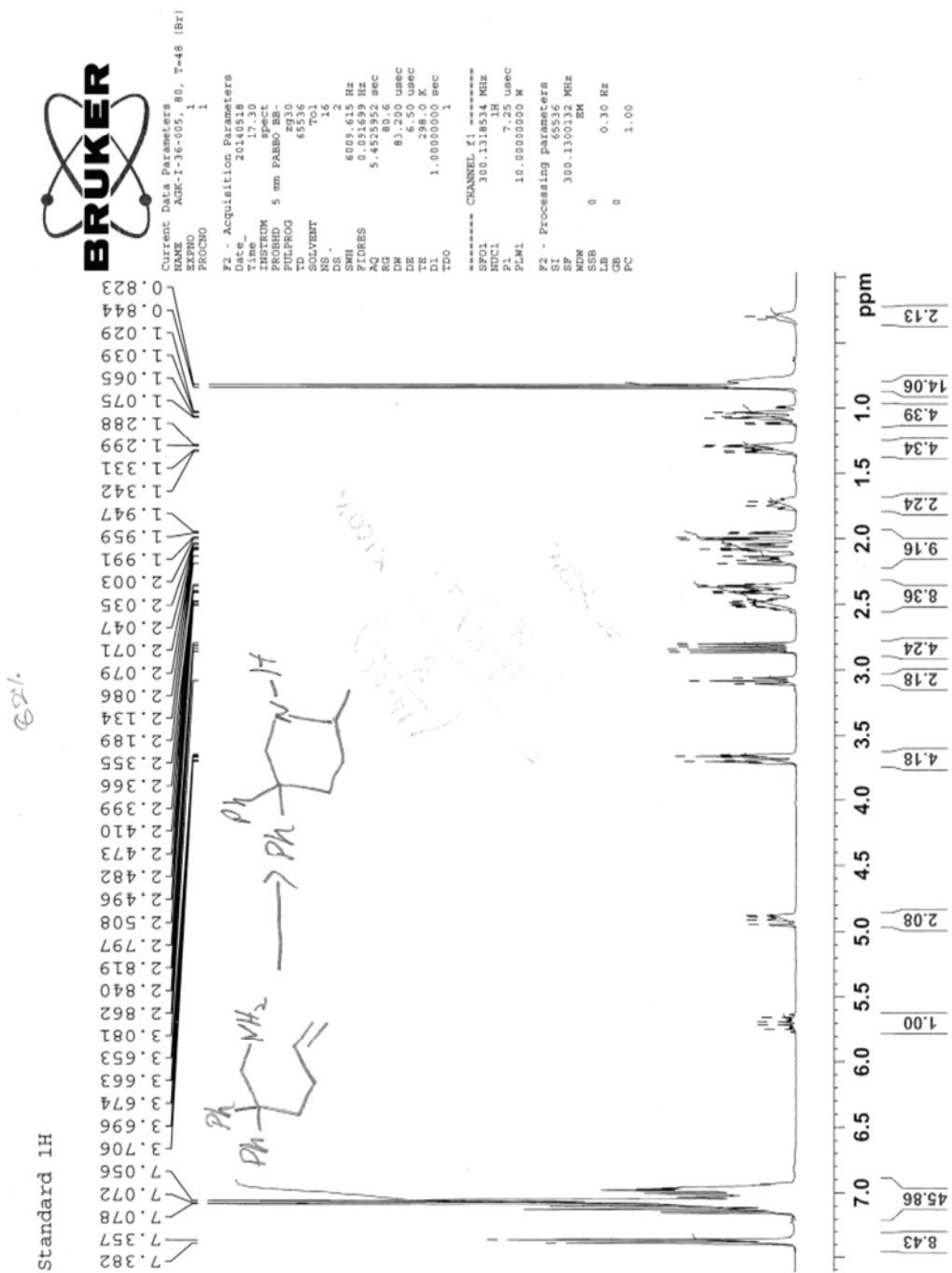
Xray data

Iodo complex **3**

<u>CRYSTAL SUMMARY</u>

Crystal data for C24 H37 I N6 Zr; M_r = 627.71; Monoclinic; space group P2$_1$/c; a = 10.3811(2) Å; b = 11.8205(2) Å; c = 21.6790(4) Å; α = 90°; β = 97.8822(8)°; γ = 90°; V = 2635.09(8) Å^3; Z = 4; T = 100(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.612 mm^{-1}; d$_{calc}$ = 1.582g.cm^{-3}; 21565 reflections collected; 4908 unique (R$_{int}$ = 0.0295); giving R$_1$ = 0.0264, wR$_2$ = 0.0666 for 4475 data with [I>2σ(I)] and R$_1$ = 0.0297, wR$_2$ = 0.0689 for all 4908 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.794/-0.738.

An arbitrary sphere of data were collected on a yellow plate-like-like crystal, having approximate dimensions of 0.150 × 0.150 × 0.100 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5° [1]. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely [2]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

<u>REFERENCES</u>

[1] Bruker AXS. (2008). *APEX-2*. Bruker-Nonius AXS, Madison, Wisconsin, USA.

[2] G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.

[3] H. D. Flack, *Acta Cryst.*, **1983**, *A39*, 876.

[4] R. W. W. Hooft, L. H. Straver & A. L. Spek, *J. Appl. Cryst.*, **2008**, *41*, 96.

[5] L. Yang, D. R. Powell & R. P. Houser, *Dalton Trans.*, **2007**, 955.

[6] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn & G. C. Verschoor, *J. Chem. Soc. Dalton Trans.*, **1984**, 1349.

Table S1. Crystal data and structure refinement for **3**.

Identification code	wdc167
Empirical formula	$C_{24} H_{37} I N_6 Zr$
Formula weight	627.71
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.3811(2)$ Å $\quad \alpha = 90°$
	$b = 11.8205(2)$ Å $\quad \beta = 97.8822(8)°$
	$c = 21.6790(4)$ Å $\quad \gamma = 90°$
Volume	$2635.09(8)$ Å^3
Z	4
Density (calculated)	1.582 g.cm^{-3}
Absorption coefficient (μ)	1.612 mm^{-1}
F(000)	1264
Crystal color, habit	yellow, plate-like
Crystal size	$0.150 \times 0.150 \times 0.100$ mm^3
θ range for data collection	1.897 to 25.623°
Index ranges	$-12 \leq h \leq 12, -12 \leq k \leq 14, -25 \leq l \leq 26$
Reflections collected	21565
Independent reflections	4908 [$R_{int} = 0.0295$]
Completeness to $\theta = 25.242°$	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6261
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4908 / 0 / 289
Goodness-of-fit on F^2	1.080
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0264$, $wR_2 = 0.0666$
R indices (all data)	$R_1 = 0.0297$, $wR_2 = 0.0689$
Extinction coefficient	n/a
Largest diff. peak and hole	0.794 and -0.738 e$^-$.Å^{-3}

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zr(1)	0.26485(3)	0.49803(2)	0.36128(2)	0.010(1)
I(1)	0.18125(2)	0.47308(2)	0.21974(2)	0.016(1)
N(1)	0.3364(2)	0.2365(2)	0.32995(11)	0.013(1)
N(2)	0.1407(2)	0.2159(2)	0.34871(11)	0.013(1)
N(3)	0.5508(2)	0.5892(2)	0.33630(11)	0.015(1)

N(4)	0.4641(2)	0.7410(2)	0.36489(12)	0.016(1)
N(5)	0.2921(2)	0.4786(2)	0.45629(12)	0.015(1)
N(6)	0.1250(2)	0.6236(2)	0.34918(11)	0.014(1)
C(1)	0.4482(3)	0.4111(3)	0.33222(13)	0.013(1)
C(2)	0.5602(3)	0.4704(3)	0.32411(14)	0.015(1)
C(3)	0.6712(3)	0.4204(3)	0.30669(14)	0.019(1)
C(4)	0.6695(3)	0.3039(3)	0.29737(14)	0.020(1)
C(5)	0.5606(3)	0.2395(3)	0.30425(14)	0.017(1)
C(6)	0.4535(3)	0.2954(3)	0.32178(13)	0.014(1)
C(7)	0.2337(3)	0.2954(2)	0.34758(13)	0.012(1)
C(8)	0.3053(3)	0.1238(3)	0.31958(14)	0.016(1)
C(9)	0.1821(3)	0.1106(3)	0.33152(14)	0.016(1)
C(10)	0.4384(3)	0.6300(3)	0.35474(13)	0.013(1)
C(11)	0.6423(3)	0.6737(3)	0.33473(14)	0.019(1)
C(12)	0.5873(3)	0.7691(3)	0.35256(15)	0.020(1)
C(13)	0.3772(3)	0.8200(3)	0.39069(15)	0.018(1)
C(14)	0.4094(3)	0.8322(3)	0.46064(14)	0.019(1)
C(15)	0.3231(3)	0.9201(3)	0.48631(15)	0.023(1)
C(16)	0.3433(4)	0.9242(4)	0.55726(17)	0.034(1)
C(17)	0.0111(3)	0.2391(3)	0.36559(14)	0.015(1)
C(18)	0.0136(3)	0.2580(3)	0.43510(14)	0.017(1)
C(19)	0.0506(3)	0.1540(3)	0.47437(15)	0.024(1)
C(20)	0.0583(4)	0.1775(3)	0.54392(15)	0.027(1)
C(21)	0.0156(3)	0.5565(3)	0.36330(16)	0.021(1)
C(22)	0.0782(3)	0.7192(3)	0.31074(15)	0.019(1)
C(23)	0.3730(3)	0.3881(3)	0.48690(15)	0.020(1)
C(24)	0.2348(3)	0.5442(3)	0.50230(15)	0.024(1)
H(3A)	0.7439	0.4634	0.3015	0.023
H(4A)	0.7429	0.2685	0.2863	0.024
H(5A)	0.5593	0.1619	0.2974	0.020
H(8A)	0.3590	0.0679	0.3068	0.020
H(9A)	0.1342	0.0438	0.3287	0.020
H(11A)	0.7252	0.6661	0.3236	0.023
H(12A)	0.6251	0.8406	0.3560	0.024
H(13A)	0.2883	0.7936	0.3807	0.022
H(13B)	0.3832	0.8935	0.3714	0.022

H(14A)	0.4997	0.8544	0.4709	0.023
H(14B)	0.3982	0.7598	0.4802	0.023
H(15A)	0.3417	0.9940	0.4702	0.028
H(15B)	0.2328	0.9026	0.4718	0.028
H(16A)	0.2872	0.9806	0.5711	0.051
H(16B)	0.4322	0.9429	0.5719	0.051
H(16C)	0.3231	0.8517	0.5734	0.051
H(17A)	-0.0458	0.1759	0.3526	0.018
H(17B)	-0.0244	0.3057	0.3433	0.018
H(18A)	0.0750	0.3180	0.4483	0.021
H(18B)	-0.0717	0.2832	0.4427	0.021
H(19A)	0.1343	0.1265	0.4657	0.028
H(19B)	-0.0131	0.0950	0.4628	0.028
H(20A)	0.0820	0.1094	0.5668	0.040
H(20B)	-0.0248	0.2032	0.5530	0.040
H(20C)	0.1225	0.2347	0.5558	0.040
H(21A)	-0.0609	0.6030	0.3598	0.032
H(21B)	0.0340	0.5275	0.4049	0.032
H(21C)	0.0014	0.4947	0.3345	0.032
H(22A)	0.0039	0.7516	0.3261	0.028
H(22B)	0.0539	0.6944	0.2686	0.028
H(22C)	0.1457	0.7750	0.3120	0.028
H(23A)	0.3737	0.3932	0.5311	0.030
H(23B)	0.4601	0.3956	0.4772	0.030
H(23C)	0.3382	0.3162	0.4724	0.030
H(24A)	0.2653	0.5159	0.5432	0.035
H(24B)	0.1418	0.5380	0.4944	0.035
H(24C)	0.2595	0.6222	0.4997	0.035

Table S3. Anisotropic displacement parameters (Å^2) for **3**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	0.0101(1)	0.0101(2)	0.0110(2)	-0.0003(1)	0.0023(1)	0.0005(1)

I(1)	0.0188(1)	0.0153(1)	0.0125(1)	-0.0014(1)	0.0006(1)	0.0037(1)
N(1)	0.0159(13)	0.0105(13)	0.0125(13)	0.0000(10)	0.0016(10)	0.0011(10)
N(2)	0.0142(12)	0.0124(13)	0.0114(13)	0.0002(10)	0.0008(10)	-0.0003(10)
N(3)	0.0144(12)	0.0157(14)	0.0142(13)	0.0009(11)	0.0023(10)	-0.0031(10)
N(4)	0.0174(13)	0.0144(14)	0.0144(13)	0.0011(11)	-0.0001(10)	-0.0030(10)
N(5)	0.0180(13)	0.0138(13)	0.0126(13)	-0.0010(10)	0.0029(10)	-0.0009(10)
N(6)	0.0138(12)	0.0131(13)	0.0142(13)	-0.0001(10)	0.0017(10)	0.0012(10)
C(1)	0.0125(14)	0.0158(16)	0.0090(14)	0.0011(12)	0.0010(11)	0.0018(11)
C(2)	0.0143(15)	0.0178(17)	0.0117(15)	0.0008(12)	0.0001(11)	0.0014(12)
C(3)	0.0128(15)	0.0283(19)	0.0161(16)	0.0013(14)	0.0016(12)	-0.0034(13)
C(4)	0.0153(15)	0.0278(19)	0.0166(16)	-0.0007(14)	0.0033(12)	0.0071(13)
C(5)	0.0179(15)	0.0164(16)	0.0155(16)	0.0011(13)	0.0013(12)	0.0060(12)
C(6)	0.0143(14)	0.0161(16)	0.0106(15)	0.0020(12)	0.0013(11)	0.0009(12)
C(7)	0.0133(14)	0.0121(15)	0.0107(14)	0.0002(12)	0.0004(11)	0.0008(11)
C(8)	0.0226(16)	0.0097(15)	0.0165(16)	-0.0008(12)	0.0023(12)	0.0027(12)
C(9)	0.0221(16)	0.0107(15)	0.0165(16)	-0.0007(12)	0.0027(12)	-0.0001(12)
C(10)	0.0148(14)	0.0135(16)	0.0106(15)	0.0001(12)	-0.0002(11)	0.0007(11)
C(11)	0.0169(15)	0.0222(18)	0.0181(16)	0.0006(13)	0.0038(12)	-0.0071(13)
C(12)	0.0225(17)	0.0187(17)	0.0196(17)	0.0015(13)	0.0027(13)	-0.0084(13)
C(13)	0.0227(16)	0.0103(16)	0.0215(17)	-0.0011(13)	-0.0001(13)	0.0008(12)
C(14)	0.0210(16)	0.0165(17)	0.0185(17)	0.0003(13)	0.0013(13)	-0.0009(13)
C(15)	0.0224(17)	0.0218(18)	0.0257(18)	-0.0028(15)	0.0046(13)	0.0010(14)
C(16)	0.035(2)	0.042(2)	0.027(2)	-0.0065(18)	0.0096(16)	0.0007(17)
C(17)	0.0124(14)	0.0127(15)	0.0203(16)	-0.0012(13)	0.0025(12)	-0.0018(11)
C(18)	0.0174(16)	0.0143(16)	0.0214(17)	-0.0016(13)	0.0063(12)	-0.0014(12)
C(19)	0.0333(19)	0.0197(18)	0.0192(17)	0.0000(14)	0.0086(14)	-0.0009(14)
C(20)	0.035(2)	0.0253(19)	0.0204(18)	0.0027(15)	0.0064(15)	-0.0021(15)
C(21)	0.0134(15)	0.0184(17)	0.0312(19)	0.0017(14)	0.0021(13)	0.0018(13)
C(22)	0.0207(16)	0.0168(17)	0.0181(17)	0.0003(13)	0.0017(12)	0.0057(13)
C(23)	0.0240(17)	0.0212(18)	0.0152(16)	0.0024(13)	0.0009(13)	0.0010(13)
C(24)	0.0310(19)	0.0235(18)	0.0180(17)	-0.0016(14)	0.0098(14)	0.0019(14)

Table S4. Bond lengths [Å] for **3**.

atom-atom	distance	atom-atom	distance
Zr(1)-N(5)	2.053(3)	Zr(1)-N(6)	2.068(2)
Zr(1)-C(1)	2.325(3)	Zr(1)-C(10)	2.402(3)
Zr(1)-C(7)	2.429(3)	Zr(1)-C(21)	2.684(3)
Zr(1)-I(1)	3.0864(3)	N(1)-C(7)	1.371(4)
N(1)-C(8)	1.382(4)	N(1)-C(6)	1.433(4)
N(2)-C(7)	1.351(4)	N(2)-C(9)	1.384(4)
N(2)-C(17)	1.468(4)	N(3)-C(10)	1.371(4)
N(3)-C(11)	1.381(4)	N(3)-C(2)	1.435(4)
N(4)-C(10)	1.351(4)	N(4)-C(12)	1.383(4)
N(4)-C(13)	1.462(4)	N(5)-C(24)	1.453(4)
N(5)-C(23)	1.462(4)	N(6)-C(22)	1.448(4)
N(6)-C(21)	1.452(4)	C(1)-C(6)	1.388(4)
C(1)-C(2)	1.390(4)	C(2)-C(3)	1.392(4)
C(3)-C(4)	1.391(5)	C(3)-H(3A)	0.9300
C(4)-C(5)	1.388(4)	C(4)-H(4A)	0.9300
C(5)-C(6)	1.390(4)	C(5)-H(5A)	0.9300
C(8)-C(9)	1.349(4)	C(8)-H(8A)	0.9300
C(9)-H(9A)	0.9300	C(11)-C(12)	1.345(5)
C(11)-H(11A)	0.9300	C(12)-H(12A)	0.9300
C(13)-C(14)	1.514(4)	C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700	C(14)-C(15)	1.525(4)
C(14)-H(14A)	0.9700	C(14)-H(14B)	0.9700
C(15)-C(16)	1.525(5)	C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700	C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600	C(16)-H(16C)	0.9600
C(17)-C(18)	1.520(4)	C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700	C(18)-C(19)	1.514(5)
C(18)-H(18A)	0.9700	C(18)-H(18B)	0.9700
C(19)-C(20)	1.524(5)	C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700	C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600	C(20)-H(20C)	0.9600
C(21)-H(21A)	0.9600	C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600	C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600	C(22)-H(22C)	0.9600
C(23)-H(23A)	0.9600	C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600	C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600	C(24)-H(24C)	0.9600

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond angles [°] for **3**.

atom-atom-atom	angle	atom-atom-atom	angle
N(5)-Zr(1)-N(6)	101.85(10)	N(5)-Zr(1)-C(1)	102.54(10)
N(6)-Zr(1)-C(1)	150.42(10)	N(5)-Zr(1)-C(10)	97.50(10)
N(6)-Zr(1)-C(10)	92.62(10)	C(1)-Zr(1)-C(10)	67.82(10)
N(5)-Zr(1)-C(7)	90.58(10)	N(6)-Zr(1)-C(7)	127.80(10)
C(1)-Zr(1)-C(7)	68.35(10)	C(10)-Zr(1)-C(7)	136.15(10)
N(5)-Zr(1)-C(21)	90.74(10)	N(6)-Zr(1)-C(21)	32.39(10)
C(1)-Zr(1)-C(21)	160.92(10)	C(10)-Zr(1)-C(21)	124.49(10)
C(7)-Zr(1)-C(21)	98.26(10)	N(5)-Zr(1)-I(1)	165.47(7)
N(6)-Zr(1)-I(1)	81.12(7)	C(1)-Zr(1)-I(1)	79.47(7)
C(10)-Zr(1)-I(1)	96.56(7)	C(7)-Zr(1)-I(1)	76.69(7)
C(21)-Zr(1)-I(1)	84.29(8)	C(7)-N(1)-C(8)	111.2(2)
C(7)-N(1)-C(6)	119.5(2)	C(8)-N(1)-C(6)	129.2(2)
C(7)-N(2)-C(9)	111.9(2)	C(7)-N(2)-C(17)	123.8(2)
C(9)-N(2)-C(17)	124.3(2)	C(10)-N(3)-C(11)	111.6(3)
C(10)-N(3)-C(2)	118.6(2)	C(11)-N(3)-C(2)	129.7(3)
C(10)-N(4)-C(12)	111.6(3)	C(10)-N(4)-C(13)	124.4(2)
C(12)-N(4)-C(13)	123.8(3)	C(24)-N(5)-C(23)	110.0(2)
C(24)-N(5)-Zr(1)	128.0(2)	C(23)-N(5)-Zr(1)	121.92(19)
C(22)-N(6)-C(21)	109.7(2)	C(22)-N(6)-Zr(1)	143.88(19)
C(21)-N(6)-Zr(1)	97.89(18)	C(6)-C(1)-C(2)	115.0(3)
C(6)-C(1)-Zr(1)	122.2(2)	C(2)-C(1)-Zr(1)	122.8(2)
C(1)-C(2)-C(3)	123.9(3)	C(1)-C(2)-N(3)	113.0(3)
C(3)-C(2)-N(3)	123.0(3)	C(4)-C(3)-C(2)	117.7(3)
C(4)-C(3)-H(3A)	121.2	C(2)-C(3)-H(3A)	121.2
C(5)-C(4)-C(3)	121.4(3)	C(5)-C(4)-H(4A)	119.3
C(3)-C(4)-H(4A)	119.3	C(4)-C(5)-C(6)	117.5(3)
C(4)-C(5)-H(5A)	121.2	C(6)-C(5)-H(5A)	121.2
C(1)-C(6)-C(5)	124.3(3)	C(1)-C(6)-N(1)	113.9(2)
C(5)-C(6)-N(1)	121.8(3)	N(2)-C(7)-N(1)	103.7(2)
N(2)-C(7)-Zr(1)	140.1(2)	N(1)-C(7)-Zr(1)	116.07(19)
C(9)-C(8)-N(1)	106.7(3)	C(9)-C(8)-H(8A)	126.7
N(1)-C(8)-H(8A)	126.7	C(8)-C(9)-N(2)	106.6(3)
C(8)-C(9)-H(9A)	126.7	N(2)-C(9)-H(9A)	126.7
N(4)-C(10)-N(3)	103.4(2)	N(4)-C(10)-Zr(1)	138.9(2)
N(3)-C(10)-Zr(1)	117.7(2)	C(12)-C(11)-N(3)	106.2(3)
C(12)-C(11)-H(11A)	126.9	N(3)-C(11)-H(11A)	126.9
C(11)-C(12)-N(4)	107.1(3)	C(11)-C(12)-H(12A)	126.4
N(4)-C(12)-H(12A)	126.4	N(4)-C(13)-C(14)	112.4(3)
N(4)-C(13)-H(13A)	109.1	C(14)-C(13)-H(13A)	109.1
N(4)-C(13)-H(13B)	109.1	C(14)-C(13)-H(13B)	109.1
H(13A)-C(13)-H(13B)	107.9	C(13)-C(14)-C(15)	111.7(3)
C(13)-C(14)-H(14A)	109.3	C(15)-C(14)-H(14A)	109.3

atom-atom-atom	angle	atom-atom-atom	angle
C(13)-C(14)-H(14B)	109.3	C(15)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	107.9	C(16)-C(15)-C(14)	112.6(3)
C(16)-C(15)-H(15A)	109.1	C(14)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15B)	109.1	C(14)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.8	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(2)-C(17)-C(18)	112.5(2)
N(2)-C(17)-H(17A)	109.1	C(18)-C(17)-H(17A)	109.1
N(2)-C(17)-H(17B)	109.1	C(18)-C(17)-H(17B)	109.1
H(17A)-C(17)-H(17B)	107.8	C(19)-C(18)-C(17)	114.0(3)
C(19)-C(18)-H(18A)	108.8	C(17)-C(18)-H(18A)	108.8
C(19)-C(18)-H(18B)	108.8	C(17)-C(18)-H(18B)	108.8
H(18A)-C(18)-H(18B)	107.7	C(18)-C(19)-C(20)	112.5(3)
C(18)-C(19)-H(19A)	109.1	C(20)-C(19)-H(19A)	109.1
C(18)-C(19)-H(19B)	109.1	C(20)-C(19)-H(19B)	109.1
H(19A)-C(19)-H(19B)	107.8	C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5	H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5	H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5	N(6)-C(21)-Zr(1)	49.72(13)
N(6)-C(21)-H(21A)	109.5	Zr(1)-C(21)-H(21A)	159.2
N(6)-C(21)-H(21B)	109.5	Zr(1)-C(21)-H(21B)	81.7
H(21A)-C(21)-H(21B)	109.5	N(6)-C(21)-H(21C)	109.5
Zr(1)-C(21)-H(21C)	81.7	H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5	N(6)-C(22)-H(22A)	109.5
N(6)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
N(6)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	N(5)-C(23)-H(23A)	109.5
N(5)-C(23)-H(23B)	109.5	H(23A)-C(23)-H(23B)	109.5
N(5)-C(23)-H(23C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5	N(5)-C(24)-H(24A)	109.5
N(5)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
N(5)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S6. Torsion angles [°] for **3**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(6)-C(1)-C(2)-C(3)	0.2(4)	Zr(1)-C(1)-C(2)-C(3)	-179.9(2)
C(6)-C(1)-C(2)-N(3)	-179.1(2)	Zr(1)-C(1)-C(2)-N(3)	0.8(4)
C(10)-N(3)-C(2)-C(1)	0.9(4)	C(11)-N(3)-C(2)-C(1)	178.2(3)
C(10)-N(3)-C(2)-C(3)	-178.4(3)	C(11)-N(3)-C(2)-C(3)	-1.1(5)
C(1)-C(2)-C(3)-C(4)	-0.5(5)	N(3)-C(2)-C(3)-C(4)	178.7(3)

C(2)-C(3)-C(4)-C(5)	0.9(5)	C(3)-C(4)-C(5)-C(6)	-1.0(5)
C(2)-C(1)-C(6)-C(5)	-0.2(4)	Zr(1)-C(1)-C(6)-C(5)	179.9(2)
C(2)-C(1)-C(6)-N(1)	-179.5(2)	Zr(1)-C(1)-C(6)-N(1)	0.6(3)
C(4)-C(5)-C(6)-C(1)	0.6(5)	C(4)-C(5)-C(6)-N(1)	179.9(3)
C(7)-N(1)-C(6)-C(1)	-1.0(4)	C(8)-N(1)-C(6)-C(1)	175.4(3)
C(7)-N(1)-C(6)-C(5)	179.7(3)	C(8)-N(1)-C(6)-C(5)	-3.9(5)
C(9)-N(2)-C(7)-N(1)	-0.9(3)	C(17)-N(2)-C(7)-N(1)	179.7(2)
C(9)-N(2)-C(7)-Zr(1)	175.0(2)	C(17)-N(2)-C(7)-Zr(1)	-4.4(5)
C(8)-N(1)-C(7)-N(2)	1.0(3)	C(6)-N(1)-C(7)-N(2)	178.0(2)
C(8)-N(1)-C(7)-Zr(1)	-176.07(19)	C(6)-N(1)-C(7)-Zr(1)	1.0(3)
C(7)-N(1)-C(8)-C(9)	-0.8(3)	C(6)-N(1)-C(8)-C(9)	-177.4(3)
N(1)-C(8)-C(9)-N(2)	0.2(3)	C(7)-N(2)-C(9)-C(8)	0.4(3)
C(17)-N(2)-C(9)-C(8)	179.9(3)	C(12)-N(4)-C(10)-N(3)	0.7(3)
C(13)-N(4)-C(10)-N(3)	-174.5(3)	C(12)-N(4)-C(10)-Zr(1)	179.8(2)
C(13)-N(4)-C(10)-Zr(1)	4.6(5)	C(11)-N(3)-C(10)-N(4)	-0.5(3)
C(2)-N(3)-C(10)-N(4)	177.2(2)	C(11)-N(3)-C(10)-Zr(1)	-179.8(2)
C(2)-N(3)-C(10)-Zr(1)	-2.1(3)	C(10)-N(3)-C(11)-C(12)	0.2(4)
C(2)-N(3)-C(11)-C(12)	-177.2(3)	N(3)-C(11)-C(12)-N(4)	0.3(3)
C(10)-N(4)-C(12)-C(11)	-0.6(4)	C(13)-N(4)-C(12)-C(11)	174.6(3)
C(10)-N(4)-C(13)-C(14)	93.9(3)	C(12)-N(4)-C(13)-C(14)	-80.7(4)
N(4)-C(13)-C(14)-C(15)	176.6(3)	C(13)-C(14)-C(15)-C(16)	173.5(3)
C(7)-N(2)-C(17)-C(18)	-73.9(4)	C(9)-N(2)-C(17)-C(18)	106.7(3)
N(2)-C(17)-C(18)-C(19)	-66.4(3)	C(17)-C(18)-C(19)-C(20)	177.3(3)
C(22)-N(6)-C(21)-Zr(1)	156.3(3)		

Symmetry transformations used to generate equivalent atoms:

Bromo complex **4**

CRYSTAL SUMMARY

Crystal data for C28 H45 Br N6 O Zr; M_r = 652.83; Monoclinic; space group P2$_1$/c; *a* = 9.0178(3) Å; *b* = 13.7634(4) Å; *c* = 24.1447(8) Å; α = 90°; β = 92.5093(16)°; γ = 90°; V = 2993.86(17) Å^3; Z = 4; T = 100(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.733 mm^{-1}; d_{calc} = 1.448g.cm^{-3}; 24368 reflections collected; 5547 unique (R_{int} = 0.0284); giving R$_1$ = 0.0390, wR$_2$ = 0.0949 for 5112 data with [I>2σ(I)] and R$_1$ = 0.0426, wR$_2$ = 0.0963 for all 5547 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.798/-0.771.

An arbitrary sphere of data were collected on a Yellow Needle-Like-like crystal, having approximate dimensions of 0.200 × 0.100 × 0.100 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5° [1]. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely [2]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

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Table S7. Crystal data and structure refinement for **4**.

Identification code	WDC168
Empirical formula	C28 H45 Br N6 O Zr
Formula weight	652.83
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2$_1$/c
Unit cell dimensions	a = 9.0178(3) Å α = 90°
	b = 13.7634(4) Å β = 92.5093(16)°
	c = 24.1447(8) Å γ = 90°
Volume	2993.86(17) Å^3
Z	4
Density (calculated)	1.448 g.cm^{-3}
Absorption coefficient (μ)	1.733 mm^{-1}
F(000)	1352
Crystal color, habit	Yellow, Needle-Like
Crystal size	0.200 × 0.100 × 0.100 mm^3
θ range for data collection	1.703 to 25.540°
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 16, -28 ≤ l ≤ 29
Reflections collected	24368
Independent reflections	5547 [R$_{int}$ = 0.0284]
Completeness to θ = 25.242°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.5984
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5547 / 0 / 340
Goodness-of-fit on F^2	1.163
Final R indices [I>2σ(I)]	R$_1$ = 0.0390, wR$_2$ = 0.0949
R indices (all data)	R$_1$ = 0.0426, wR$_2$ = 0.0963
Extinction coefficient	0
Largest diff. peak and hole	0.798 and -0.771 e$^-$.Å^{-3}

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Zr(1)	0.43694(4)	0.34668(2)	0.35257(2)	0.016(1)
Br(1)	0.29657(4)	0.35563(2)	0.24654(2)	0.021(1)
O(1)	0.1095(6)	0.8081(3)	0.4275(2)	0.082(1)
N(1)	0.7147(3)	0.2757(2)	0.28098(13)	0.020(1)
N(2)	0.6149(3)	0.1407(2)	0.30165(12)	0.019(1)
N(3)	0.5166(3)	0.5766(2)	0.33526(12)	0.019(1)
N(4)	0.3284(3)	0.5871(2)	0.38539(13)	0.020(1)
N(5)	0.2424(3)	0.2772(2)	0.37850(13)	0.024(1)
N(6)	0.5734(3)	0.3253(2)	0.42148(13)	0.021(1)
C(1)	0.6198(4)	0.4294(2)	0.30556(15)	0.019(1)
C(2)	0.6315(4)	0.5298(3)	0.30552(15)	0.019(1)
C(3)	0.7427(4)	0.5813(3)	0.28027(16)	0.022(1)
C(4)	0.8500(4)	0.5276(3)	0.25444(17)	0.025(1)
C(5)	0.8474(4)	0.4263(3)	0.25399(17)	0.025(1)
C(6)	0.7310(4)	0.3810(3)	0.27891(15)	0.020(1)
C(7)	0.5983(4)	0.2377(3)	0.30759(15)	0.019(1)
C(8)	0.8018(4)	0.2039(3)	0.25924(16)	0.022(1)
C(9)	0.7387(4)	0.1190(3)	0.27232(16)	0.022(1)
C(10)	0.4141(4)	0.5202(3)	0.36107(15)	0.019(1)
C(11)	0.4934(4)	0.6745(3)	0.34377(16)	0.023(1)
C(12)	0.3742(4)	0.6813(3)	0.37548(16)	0.023(1)
C(13)	0.1963(4)	0.5634(3)	0.41644(16)	0.022(1)
C(14)	0.0627(4)	0.5422(3)	0.37838(17)	0.029(1)
C(15)	-0.0732(5)	0.5137(3)	0.41072(19)	0.038(1)
C(16)	-0.1475(5)	0.5987(4)	0.4376(2)	0.051(1)
C(17)	0.5166(4)	0.0685(3)	0.32594(15)	0.021(1)
C(18)	0.5859(4)	0.0214(3)	0.37761(16)	0.026(1)
C(19)	0.4797(5)	-0.0513(3)	0.40191(17)	0.033(1)
C(20)	0.5486(6)	-0.1073(3)	0.4506(2)	0.045(1)
C(21)	0.2469(5)	0.2189(3)	0.42912(18)	0.036(1)
C(22)	0.0923(4)	0.2702(3)	0.3542(2)	0.038(1)

C(23)	0.7156(4)	0.2809(3)	0.43525(17)	0.027(1)
C(24)	0.5177(5)	0.3740(3)	0.46975(17)	0.029(1)
C(25)	0.0784(10)	0.8813(6)	0.4669(3)	0.099(3)
C(26)	-0.0085(8)	0.9601(6)	0.4364(3)	0.081(2)
C(27)	0.0175(7)	0.9422(5)	0.3763(3)	0.067(2)
C(28)	0.0381(12)	0.8330(6)	0.3757(3)	0.109(3)
H(3A)	0.7451	0.6503	0.2807	0.026
H(4A)	0.9271	0.5606	0.2366	0.030
H(5A)	0.9228	0.3899	0.2372	0.031
H(8A)	0.8889	0.2128	0.2391	0.026
H(9A)	0.7728	0.0560	0.2631	0.026
H(11A)	0.5501	0.7267	0.3300	0.027
H(12A)	0.3303	0.7394	0.3884	0.028
H(13A)	0.1733	0.6186	0.4409	0.026
H(13B)	0.2179	0.5060	0.4402	0.026
H(14A)	0.0870	0.4886	0.3529	0.035
H(14B)	0.0388	0.6004	0.3557	0.035
H(15A)	-0.1463	0.4812	0.3851	0.045
H(15B)	-0.0423	0.4663	0.4398	0.045
H(16A)	-0.2333	0.5756	0.4574	0.076
H(16B)	-0.1806	0.6454	0.4090	0.076
H(16C)	-0.0768	0.6303	0.4638	0.076
H(17A)	0.4923	0.0176	0.2981	0.026
H(17B)	0.4227	0.1006	0.3354	0.026
H(18A)	0.6115	0.0721	0.4055	0.032
H(18B)	0.6786	-0.0122	0.3682	0.032
H(19A)	0.3909	-0.0163	0.4141	0.039
H(19B)	0.4466	-0.0979	0.3726	0.039
H(20A)	0.4729	-0.1482	0.4669	0.067
H(20B)	0.5882	-0.0615	0.4786	0.067
H(20C)	0.6291	-0.1483	0.4379	0.067
H(21A)	0.2141	0.1526	0.4203	0.054
H(21B)	0.1810	0.2477	0.4558	0.054
H(21C)	0.3486	0.2174	0.4451	0.054
H(22A)	0.0220	0.2964	0.3802	0.056
H(22B)	0.0685	0.2019	0.3464	0.056

H(22C)	0.0852	0.3074	0.3196	0.056
H(23A)	0.7037	0.2314	0.4639	0.041
H(23B)	0.7856	0.3307	0.4491	0.041
H(23C)	0.7538	0.2504	0.4021	0.041
H(24A)	0.5131	0.3276	0.5004	0.043
H(24B)	0.4182	0.3997	0.4607	0.043
H(24C)	0.5843	0.4276	0.4807	0.043
H(25A)	0.1719	0.9080	0.4836	0.118
H(25B)	0.0195	0.8539	0.4968	0.118
H(26A)	-0.1155	0.9554	0.4436	0.097
H(26B)	0.0279	1.0252	0.4479	0.097
H(27A)	0.1074	0.9764	0.3645	0.081
H(27B)	-0.0689	0.9624	0.3524	0.081
H(28A)	-0.0592	0.7999	0.3712	0.131
H(28B)	0.1001	0.8136	0.3447	0.131

Table S9. Anisotropic displacement parameters ($\mathring{A}^2$) for **4**.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	0.0168(2)	0.0115(2)	0.0204(2)	0.0007(1)	-0.0022(1)	-0.0005(1)
Br(1)	0.0248(2)	0.0140(2)	0.0233(2)	-0.0007(1)	-0.0055(1)	0.0010(1)
O(1)	0.103(4)	0.068(3)	0.075(3)	0.013(2)	0.003(3)	0.035(3)
N(1)	0.0184(15)	0.0136(15)	0.0263(17)	0.0022(12)	-0.0032(12)	0.0022(12)
N(2)	0.0213(15)	0.0147(15)	0.0199(16)	0.0017(12)	-0.0046(12)	0.0015(12)
N(3)	0.0196(15)	0.0123(14)	0.0233(16)	0.0000(12)	-0.0049(12)	-0.0012(11)
N(4)	0.0209(15)	0.0160(15)	0.0234(17)	-0.0005(12)	-0.0019(13)	-0.0016(12)
N(5)	0.0202(15)	0.0222(16)	0.0286(18)	0.0014(14)	-0.0010(13)	-0.0036(13)
N(6)	0.0237(16)	0.0160(15)	0.0215(16)	0.0004(12)	-0.0022(12)	-0.0018(12)
C(1)	0.0185(17)	0.0150(17)	0.0215(19)	0.0000(14)	-0.0054(14)	-0.0021(14)
C(2)	0.0187(17)	0.0185(18)	0.0201(19)	0.0003(14)	-0.0058(14)	0.0001(14)
C(3)	0.0212(18)	0.0141(17)	0.030(2)	0.0018(15)	-0.0066(15)	-0.0011(14)
C(4)	0.0181(18)	0.0202(19)	0.037(2)	0.0041(17)	0.0001(16)	-0.0051(15)

C(5)	0.0200(18)	0.0204(19)	0.036(2)	0.0001(17)	0.0002(16)	0.0028(15)
C(6)	0.0189(17)	0.0165(17)	0.0240(19)	-0.0009(15)	-0.0048(14)	-0.0031(14)
C(7)	0.0196(17)	0.0148(17)	0.0221(19)	-0.0001(14)	-0.0063(14)	-0.0003(14)
C(8)	0.0192(18)	0.0208(19)	0.026(2)	-0.0005(15)	-0.0007(15)	0.0063(15)
C(9)	0.0228(18)	0.0170(18)	0.026(2)	-0.0023(15)	-0.0023(15)	0.0061(14)
C(10)	0.0185(17)	0.0168(17)	0.0214(19)	0.0018(14)	-0.0050(14)	-0.0015(14)
C(11)	0.0276(19)	0.0100(16)	0.030(2)	0.0000(15)	-0.0045(16)	-0.0017(14)
C(12)	0.0274(19)	0.0117(17)	0.030(2)	-0.0026(15)	-0.0031(16)	0.0024(15)
C(13)	0.0229(18)	0.0194(18)	0.024(2)	-0.0002(15)	-0.0003(15)	-0.0003(15)
C(14)	0.026(2)	0.033(2)	0.028(2)	-0.0008(17)	-0.0027(16)	-0.0018(17)
C(15)	0.030(2)	0.045(3)	0.037(3)	0.008(2)	-0.0066(19)	-0.009(2)
C(16)	0.034(3)	0.073(4)	0.045(3)	0.002(3)	0.008(2)	0.005(2)
C(17)	0.0247(19)	0.0138(17)	0.025(2)	0.0020(15)	-0.0034(15)	-0.0028(14)
C(18)	0.034(2)	0.0200(19)	0.025(2)	0.0035(16)	-0.0071(17)	-0.0028(16)
C(19)	0.046(2)	0.022(2)	0.029(2)	0.0042(17)	-0.0027(19)	-0.0082(18)
C(20)	0.069(3)	0.032(2)	0.034(3)	0.012(2)	-0.002(2)	-0.005(2)
C(21)	0.039(2)	0.036(2)	0.033(2)	0.0098(19)	0.0001(19)	-0.016(2)
C(22)	0.025(2)	0.038(3)	0.049(3)	0.008(2)	-0.0010(19)	-0.0059(18)
C(23)	0.0237(19)	0.029(2)	0.029(2)	-0.0002(17)	-0.0065(16)	0.0001(16)
C(24)	0.035(2)	0.026(2)	0.026(2)	-0.0028(17)	-0.0062(17)	0.0046(17)
C(25)	0.113(6)	0.100(6)	0.085(6)	0.034(5)	0.032(5)	0.055(5)
C(26)	0.075(4)	0.078(5)	0.089(5)	0.020(4)	-0.003(4)	0.016(4)
C(27)	0.063(4)	0.071(4)	0.067(4)	0.018(3)	0.004(3)	0.014(3)
C(28)	0.170(9)	0.072(5)	0.081(5)	0.022(4)	-0.033(6)	0.035(5)

Table S10. Bond lengths [Å] for **4**.

atom-atom	distance	atom-atom	distance
Zr(1)-N(6)	2.047(3)	Zr(1)-N(5)	2.116(3)
Zr(1)-C(1)	2.339(4)	Zr(1)-C(7)	2.384(4)
Zr(1)-C(10)	2.407(4)	Zr(1)-Br(1)	2.8087(5)
O(1)-C(25)	1.422(9)	O(1)-C(28)	1.423(8)
N(1)-C(7)	1.359(5)	N(1)-C(8)	1.380(5)
N(1)-C(6)	1.457(4)	N(2)-C(7)	1.352(4)
N(2)-C(9)	1.380(5)	N(2)-C(17)	1.470(5)
N(3)-C(10)	1.377(5)	N(3)-C(11)	1.381(4)
N(3)-C(2)	1.438(5)	N(4)-C(10)	1.352(5)
N(4)-C(12)	1.385(5)	N(4)-C(13)	1.472(5)

atom-atom	distance	atom-atom	distance
N(5)-C(22)	1.455(5)	N(5)-C(21)	1.461(5)
N(6)-C(23)	1.446(5)	N(6)-C(24)	1.453(5)
C(1)-C(2)	1.385(5)	C(1)-C(6)	1.386(5)
C(2)-C(3)	1.391(5)	C(3)-C(4)	1.387(5)
C(3)-H(3A)	0.9500	C(4)-C(5)	1.394(5)
C(4)-H(4A)	0.9500	C(5)-C(6)	1.382(5)
C(5)-H(5A)	0.9500	C(8)-C(9)	1.344(5)
C(8)-H(8A)	0.9500	C(9)-H(9A)	0.9500
C(11)-C(12)	1.350(5)	C(11)-H(11A)	0.9500
C(12)-H(12A)	0.9500	C(13)-C(14)	1.511(5)
C(13)-H(13A)	0.9900	C(13)-H(13B)	0.9900
C(14)-C(15)	1.533(6)	C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900	C(15)-C(16)	1.508(7)
C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9800	C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800	C(17)-C(18)	1.516(5)
C(17)-H(17A)	0.9900	C(17)-H(17B)	0.9900
C(18)-C(19)	1.521(5)	C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900	C(19)-C(20)	1.516(6)
C(19)-H(19A)	0.9900	C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800	C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800	C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800	C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800	C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800	C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800	C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800	C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800	C(25)-C(26)	1.511(9)
C(25)-H(25A)	0.9900	C(25)-H(25B)	0.9900
C(26)-C(27)	1.499(9)	C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900	C(27)-C(28)	1.514(10)
C(27)-H(27A)	0.9900	C(27)-H(27B)	0.9900
C(28)-H(28A)	0.9900	C(28)-H(28B)	0.9900

Symmetry transformations used to generate equivalent atoms:

Table S11. Bond angles [°] for **4**.

atom-atom-atom	angle	atom-atom-atom	angle
N(6)-Zr(1)-N(5)	99.88(12)	N(6)-Zr(1)-C(1)	93.02(12)
N(5)-Zr(1)-C(1)	167.10(12)	N(6)-Zr(1)-C(7)	85.57(12)
N(5)-Zr(1)-C(7)	112.39(12)	C(1)-Zr(1)-C(7)	68.16(12)
N(6)-Zr(1)-C(10)	97.11(12)	N(5)-Zr(1)-C(10)	110.35(12)
C(1)-Zr(1)-C(10)	67.84(12)	C(7)-Zr(1)-C(10)	136.00(12)

N(6)-Zr(1)-Br(1)	168.01(9)	N(5)-Zr(1)-Br(1)	86.74(9)
C(1)-Zr(1)-Br(1)	80.53(8)	C(7)-Zr(1)-Br(1)	82.65(8)
C(10)-Zr(1)-Br(1)	89.84(8)	C(25)-O(1)-C(28)	108.8(5)
C(7)-N(1)-C(8)	111.6(3)	C(7)-N(1)-C(6)	118.7(3)
C(8)-N(1)-C(6)	129.7(3)	C(7)-N(2)-C(9)	111.3(3)
C(7)-N(2)-C(17)	123.6(3)	C(9)-N(2)-C(17)	125.0(3)
C(10)-N(3)-C(11)	111.9(3)	C(10)-N(3)-C(2)	119.1(3)
C(11)-N(3)-C(2)	129.0(3)	C(10)-N(4)-C(12)	112.5(3)
C(10)-N(4)-C(13)	124.1(3)	C(12)-N(4)-C(13)	123.3(3)
C(22)-N(5)-C(21)	107.0(3)	C(22)-N(5)-Zr(1)	132.8(3)
C(21)-N(5)-Zr(1)	120.2(2)	C(23)-N(6)-C(24)	110.2(3)
C(23)-N(6)-Zr(1)	138.0(3)	C(24)-N(6)-Zr(1)	111.7(2)
C(2)-C(1)-C(6)	115.0(3)	C(2)-C(1)-Zr(1)	122.8(3)
C(6)-C(1)-Zr(1)	122.1(2)	C(1)-C(2)-C(3)	124.4(3)
C(1)-C(2)-N(3)	113.0(3)	C(3)-C(2)-N(3)	122.6(3)
C(4)-C(3)-C(2)	117.1(3)	C(4)-C(3)-H(3A)	121.5
C(2)-C(3)-H(3A)	121.5	C(3)-C(4)-C(5)	121.7(4)
C(3)-C(4)-H(4A)	119.2	C(5)-C(4)-H(4A)	119.2
C(6)-C(5)-C(4)	117.4(4)	C(6)-C(5)-H(5A)	121.3
C(4)-C(5)-H(5A)	121.3	C(5)-C(6)-C(1)	124.3(3)
C(5)-C(6)-N(1)	122.9(3)	C(1)-C(6)-N(1)	112.7(3)
N(2)-C(7)-N(1)	103.8(3)	N(2)-C(7)-Zr(1)	137.9(3)
N(1)-C(7)-Zr(1)	118.2(2)	C(9)-C(8)-N(1)	106.2(3)
C(9)-C(8)-H(8A)	126.9	N(1)-C(8)-H(8A)	126.9
C(8)-C(9)-N(2)	107.0(3)	C(8)-C(9)-H(9A)	126.5
N(2)-C(9)-H(9A)	126.5	N(4)-C(10)-N(3)	102.8(3)
N(4)-C(10)-Zr(1)	139.9(3)	N(3)-C(10)-Zr(1)	117.3(2)
C(12)-C(11)-N(3)	106.4(3)	C(12)-C(11)-H(11A)	126.8
N(3)-C(11)-H(11A)	126.8	C(11)-C(12)-N(4)	106.5(3)
C(11)-C(12)-H(12A)	126.8	N(4)-C(12)-H(12A)	126.8
N(4)-C(13)-C(14)	112.0(3)	N(4)-C(13)-H(13A)	109.2
C(14)-C(13)-H(13A)	109.2	N(4)-C(13)-H(13B)	109.2
C(14)-C(13)-H(13B)	109.2	H(13A)-C(13)-H(13B)	107.9
C(13)-C(14)-C(15)	111.9(3)	C(13)-C(14)-H(14A)	109.2
C(15)-C(14)-H(14A)	109.2	C(13)-C(14)-H(14B)	109.2
C(15)-C(14)-H(14B)	109.2	H(14A)-C(14)-H(14B)	107.9
C(16)-C(15)-C(14)	113.6(4)	C(16)-C(15)-H(15A)	108.8
C(14)-C(15)-H(15A)	108.8	C(16)-C(15)-H(15B)	108.8
C(14)-C(15)-H(15B)	108.8	H(15A)-C(15)-H(15B)	107.7
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(2)-C(17)-C(18)	112.5(3)	N(2)-C(17)-H(17A)	109.1
C(18)-C(17)-H(17A)	109.1	N(2)-C(17)-H(17B)	109.1
C(18)-C(17)-H(17B)	109.1	H(17A)-C(17)-H(17B)	107.8
C(17)-C(18)-C(19)	110.8(3)	C(17)-C(18)-H(18A)	109.5

C(19)-C(18)-H(18A)	109.5	C(17)-C(18)-H(18B)	109.5
C(19)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18B)	108.1
C(20)-C(19)-C(18)	112.9(4)	C(20)-C(19)-H(19A)	109.0
C(18)-C(19)-H(19A)	109.0	C(20)-C(19)-H(19B)	109.0
C(18)-C(19)-H(19B)	109.0	H(19A)-C(19)-H(19B)	107.8
C(19)-C(20)-H(20A)	109.5	C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5	C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5	H(20B)-C(20)-H(20C)	109.5
N(5)-C(21)-H(21A)	109.5	N(5)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5	N(5)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(21B)-C(21)-H(21C)	109.5
N(5)-C(22)-H(22A)	109.5	N(5)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5	N(5)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5	H(22B)-C(22)-H(22C)	109.5
N(6)-C(23)-H(23A)	109.5	N(6)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5	N(6)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(23B)-C(23)-H(23C)	109.5
N(6)-C(24)-H(24A)	109.5	N(6)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5	N(6)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(24B)-C(24)-H(24C)	109.5
O(1)-C(25)-C(26)	107.2(6)	O(1)-C(25)-H(25A)	110.3
C(26)-C(25)-H(25A)	110.3	O(1)-C(25)-H(25B)	110.3
C(26)-C(25)-H(25B)	110.3	H(25A)-C(25)-H(25B)	108.5
C(27)-C(26)-C(25)	104.7(6)	C(27)-C(26)-H(26A)	110.8
C(25)-C(26)-H(26A)	110.8	C(27)-C(26)-H(26B)	110.8
C(25)-C(26)-H(26B)	110.8	H(26A)-C(26)-H(26B)	108.9
C(26)-C(27)-C(28)	101.4(6)	C(26)-C(27)-H(27A)	111.5
C(28)-C(27)-H(27A)	111.5	C(26)-C(27)-H(27B)	111.5
C(28)-C(27)-H(27B)	111.5	H(27A)-C(27)-H(27B)	109.3
O(1)-C(28)-C(27)	106.3(6)	O(1)-C(28)-H(28A)	110.5
C(27)-C(28)-H(28A)	110.5	O(1)-C(28)-H(28B)	110.5
C(27)-C(28)-H(28B)	110.5	H(28A)-C(28)-H(28B)	108.7

Symmetry transformations used to generate equivalent atoms:

Table S12. Torsion angles [°] for **4**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(6)-C(1)-C(2)-C(3)	1.2(5)	Zr(1)-C(1)-C(2)-C(3)	176.8(3)
C(6)-C(1)-C(2)-N(3)	-178.0(3)	Zr(1)-C(1)-C(2)-N(3)	-2.4(4)
C(10)-N(3)-C(2)-C(1)	1.9(4)	C(11)-N(3)-C(2)-C(1)	180.0(3)
C(10)-N(3)-C(2)-C(3)	-177.3(3)	C(11)-N(3)-C(2)-C(3)	0.8(6)
C(1)-C(2)-C(3)-C(4)	-1.2(6)	N(3)-C(2)-C(3)-C(4)	177.9(3)
C(2)-C(3)-C(4)-C(5)	-0.4(6)	C(3)-C(4)-C(5)-C(6)	1.9(6)
C(4)-C(5)-C(6)-C(1)	-2.0(6)	C(4)-C(5)-C(6)-N(1)	179.6(3)
C(2)-C(1)-C(6)-C(5)	0.5(5)	Zr(1)-C(1)-C(6)-C(5)	-175.2(3)
C(2)-C(1)-C(6)-N(1)	179.0(3)	Zr(1)-C(1)-C(6)-N(1)	3.4(4)
C(7)-N(1)-C(6)-C(5)	178.4(3)	C(8)-N(1)-C(6)-C(5)	-1.8(6)
C(7)-N(1)-C(6)-C(1)	-0.1(5)	C(8)-N(1)-C(6)-C(1)	179.7(3)
C(9)-N(2)-C(7)-N(1)	0.2(4)	C(17)-N(2)-C(7)-N(1)	177.5(3)
C(9)-N(2)-C(7)-Zr(1)	-176.4(3)	C(17)-N(2)-C(7)-Zr(1)	0.9(6)
C(8)-N(1)-C(7)-N(2)	-0.2(4)	C(6)-N(1)-C(7)-N(2)	179.6(3)
C(8)-N(1)-C(7)-Zr(1)	177.2(2)	C(6)-N(1)-C(7)-Zr(1)	-3.0(4)
C(7)-N(1)-C(8)-C(9)	0.1(4)	C(6)-N(1)-C(8)-C(9)	-179.7(3)
N(1)-C(8)-C(9)-N(2)	0.0(4)	C(7)-N(2)-C(9)-C(8)	-0.1(4)
C(17)-N(2)-C(9)-C(8)	-177.4(3)	C(12)-N(4)-C(10)-N(3)	0.1(4)
C(13)-N(4)-C(10)-N(3)	176.9(3)	C(12)-N(4)-C(10)-Zr(1)	178.8(3)
C(13)-N(4)-C(10)-Zr(1)	-4.3(6)	C(11)-N(3)-C(10)-N(4)	0.0(4)
C(2)-N(3)-C(10)-N(4)	178.4(3)	C(11)-N(3)-C(10)-Zr(1)	-179.1(2)
C(2)-N(3)-C(10)-Zr(1)	-0.7(4)	C(10)-N(3)-C(11)-C(12)	0.0(4)
C(2)-N(3)-C(11)-C(12)	-178.2(3)	N(3)-C(11)-C(12)-N(4)	0.1(4)
C(10)-N(4)-C(12)-C(11)	-0.1(4)	C(13)-N(4)-C(12)-C(11)	-177.0(3)
C(10)-N(4)-C(13)-C(14)	-78.7(4)	C(12)-N(4)-C(13)-C(14)	97.8(4)
N(4)-C(13)-C(14)-C(15)	177.8(3)	C(13)-C(14)-C(15)-C(16)	76.1(5)
C(7)-N(2)-C(17)-C(18)	-102.5(4)	C(9)-N(2)-C(17)-C(18)	74.4(4)
N(2)-C(17)-C(18)-C(19)	179.0(3)	C(17)-C(18)-C(19)-C(20)	174.8(4)
C(28)-O(1)-C(25)-C(26)	-4.4(9)	O(1)-C(25)-C(26)-C(27)	-17.2(9)
C(25)-C(26)-C(27)-C(28)	30.3(8)	C(25)-O(1)-C(28)-C(27)	24.3(10)
C(26)-C(27)-C(28)-O(1)	-33.8(9)		

Symmetry transformations used to generate equivalent atoms: