Electronic Supplementary Information

Zinc(II) *ortho*-Hydroxyphenylhydrazo-β-diketonate Complexes and their Catalytic Ability towards Diastereoselective Nitroaldol (Henry) Reaction

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Analytical data for compounds 1−4.

1: Yield: 72 % (based on pentane-2,4-dione), black powder soluble in methanol, ethanol, acetone and insoluble in water and chloroform. Anal. Calcd for $C_{11}H_{12}N_2O_3$ (M = 220): C, 60.00; H, 5.45; N, 12.73. Found: C, 58.88; H, 5.47; N, 12.20. IR (KBr, selected bands, cm^{-1}): 3468 (NH), 3079 (OH), 1668 (C=O), 1632 (C=O···H), 1599 (C=N). ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 2.41 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 6.91-7.67 (4H, Ar−H), 10.51 (s, 1H, OH), 14.58 (s, 1H, NH). ^{13}C{^{1}H} NMR 75.468 MHz, DMSO-d_6), δ: 26.5 (CH_3), 31.2 (CH_3), 114.9, 115.8, 120.2, and 126.2 (C_{Ar-H}), 129.3 ($C_{Ar-NH-N}$), 133.2 (C=N), 146.3 (C_{Ar-OH}), 196.2 and 196.4 (C=O).

2: Yield: 85.0 % (based on pentane-2,4-dione), dark brown powder, soluble in ethanol, acetone and methanol and insoluble in water and chloroform. Anal. Calcd for $C_{11}H_{11}N_3O_5$ (M=265.22): C, 49.81; H, 4.18; N, 15.84. Found: C, 49.85; H, 4.17; N, 15.39. IR (KBr, selected bands, cm^{-1}): 3461 (s, br) ν(OH), 3095 (s, br) ν(NH), 1638 (s) ν(C=O), 1626 (s) ν(C=O···H), 1598 (s) ν(C=N) cm^{-1}. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ = 2.45 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 7.73−7.86 (m, 3H, Ar−H), 11.55 (s, 1H, OH), 14.17 (s, 1H, NH). ^{13}C{^{1}H} (75.468 MHz, DMSO-d_6): δ= 26.55 (CH_3), 31.38 (CH_3), 110.21 (Ar−H), 114.31 (Ar−H), 116.30 (Ar−H), 135.38 (C=N), 136.02 (Ar−NO_2), 143.65 (Ar−NH−N), 145.72 (Ar−OH), 196.52 (C=O), 197.44 (C=O) ppm.

3: Yield: 75 % (based on 5,5-dimethylcyclohexane-1,3-dione), dark brown powder soluble in methanol, ethanol, acetone and insoluble in water and chloroform. Anal. Calcd for $C_{14}H_{16}N_2O_3$ (M = 260): C, 64.61; H, 6.15; N, 10.78. Found: C, 64.09; H, 6.38; N, 10.70. IR (KBr, selected bands, cm^{-1}): 3180 (NH), 2952 (OH), 1650 (C=O), 1616 (C=O···H), 1594 (C=N). ^{1}H NMR (300.13 MHz, DMSO-d_6), δ: 1.02 (s, 6H, CH_3), 2.50 (s, 2H, CH_2), 2.57 (s, 2H, CH_2), 6.92-7.64 (3H, Ar–H), 10.75 (s, 1H, OH), 15.25 (s, 1H, NH). ^{13}C{^{1}H} NMR 75.468 MHz, DMSO-d_6), δ: 28.0 (CH_3), 30.4 (CH_3), 51.8 (CH_2), 51.8 (CH_2), 38.9 (C_{ipso}), 116.0, 120.3, 127.3 and 128.0 (C_{Ar-H}), 130.3 ($C_{Ar-NH-N}$), 137.0 (C=N), 147.2 (C_{Ar-OH}), 204.2 and 206.0 (C=O).

4: Yield: 83 % (based on 5,5-dimethylcyclohexane-1,3-dione), dark brown powder soluble in methanol, ethanol, acetone and insoluble in water and chloroform. Anal. Calcd for $C_{14}H_{15}N_3O_5$ (M = 305): C, 55.08; H, 4.92; N, 13.77. Found: C, 55.00; H, 4.98; N, 13.68. IR (KBr, selected bands, cm^{-1}): 3448 (NH), 3100 (OH), 1665 (C=O), 1628 (C=O···H), 1596 (C=N). ^{1}H NMR (400.13 MHz, DMSO-d_6), δ: 0.90-1.03 (s, 6H, CH_3), 2.50 (s, 2H, CH_2), 2.62 (s, 2H, CH_2), 7.22-7.74 (3H, Ar−H), 10.27 (s, 1H, OH), 14.91 (s, 1H, NH). ^{13}C{^{1}H} NMR (100.61 MHz, DMSO-d_6), δ: 28.0 (CH_3), 30.3 (CH_3), 52.0 (CH_2), 52.0 (CH_2), 38.7 (C_{ipso}), 110.7, 114.5, and 115.3 (C_{Ar-H}), 131.7 ($C_{Ar-NH-N}$), 136.1 (C=N), 144.8 (C_{Ar-NO2}), 149.0 (C_{Ar-OH}), 203.4 and 206.3 (C=O).

X-ray data of 5−8

Table S1. Selected bond distances (Å) and angles (°) for compounds **5** − **8**.

	5	**6**	**7**	**8**
	Coordinated ligand			
C–O (*coordinated carbonyl*)	1.264(3)	1.246(7)	1.255(4)	1.279(18)
C–O (*free carbonyl*)	1.236(4)	1.240(7)	1.242(4)	1.222(18)
N–N	1.283(3)	1.281(6)	1.276(3)	1.287(17)
	Coordination sphere of Zn			
Zn–N	2.019(2)	2.032(5)	2.052(2)	2.065(14)
∠ (axial sites)	166.23(8)	163.56(17)	161.60(10)	166.0(4)
∠ (equatorial sites)	103.86(9) | 127.15(9)	104.3(2) | 133.3(2)	101.47(9) | 139.39(9)	104.6(5) | 132.1(5)
	Zn(μ-O)$_2$Zn core			
∠ ZnOZn	98.16(8)	-	102.22(9)	-
∠ OZnO	81.84(8)	-	77.78(9)	-
Longest Zn–O	2.109(2)	-	2.086(2)	-
Shortest Zn–O	1.986(2)	-	1.966(2)	-
Zn–Zn	3.0955(7)	-	3.1551(7)	-
	6-membered metallacycle			
∠ OZnN	86.38(9)	83.86(19)	87.05(9)	85.1(4)
Zn–O	2.025(2)	2.046(4)	2.018(2)	2.024(9)
	5-membered metallacycle			
∠ OZnN	80.03(9)	80.74(18)	79.74(8)	81.9(5)
Zn–O$_{ortho}$	2.109(2)	2.037(4)	2.086(2)	1.999(10)

Table S2. Relevant hydrogen bonding distances (Å) and angles (º) [d(D···A) / ∠(D–H···A)] in **5** – **8**.

Compound	D–H···A	d(D···A)	∠(D–H···A)	Symmetry codes
5	O4–H4···O2^{i}	2.629(4)	178(5)	*i:* 1-x,1-y,1-z
6	O10–H10A···O11^{i}	2.542(6)	150	*i*: 1-x,-y,1-z
	O10–H10B···O4^{ii}	2.687(8)	170	*ii*: 1-x,1-y,2-z
7	O10–H10A···O3^{i}	2.696(3)	166(3)	*i:* 2-x,2-y,-z
	O10–H10C···O3^{ii}	2.695(3)	157(3)	*ii:* -1+x,y,z
8	O10–H10B···O3	2.70(2)	132	
	O10–H10A···O3^{i}	2.702(16)	129	*i:* 1-x,1/2+y,1/2-z
	O11–H11B···O10^{ii}	2.62(2)	163	*ii:* 2-x,1/2+y,1/2-z
	O12–H12A···O1^{iii}	2.526(15)	159	*iii:* 2-x,1-y,1-z
	O12–H12B···O10^{iv}	2.911(19)	143	*iv:* x,1/2-y,1/2+z

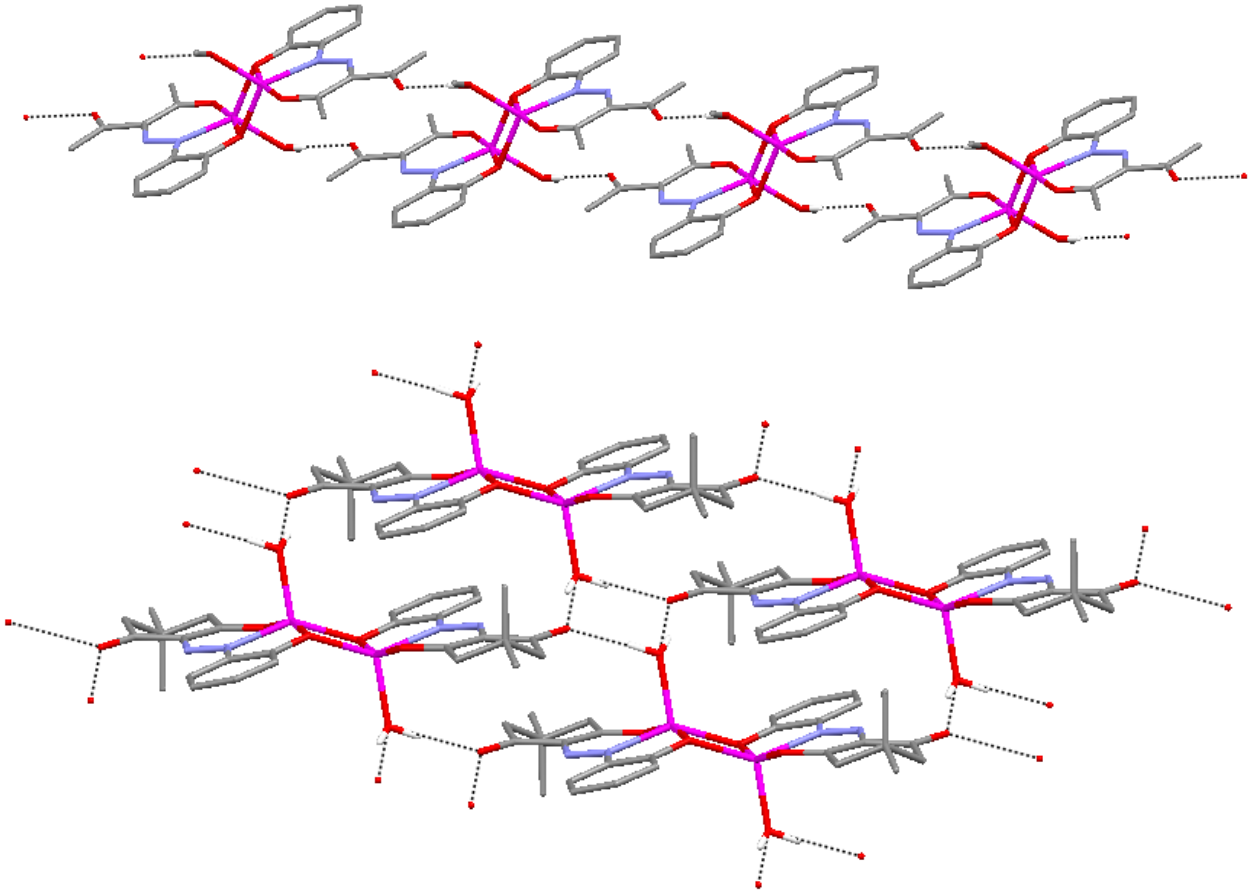


Figure S1. Fragments of the crystal packing diagram of **5** (top) and **7** (down) showing the relative arrangement of four zinc dimers which are assembled into 1D chains (**5**) or 2D layers (**7**) *via* hydrogen bonds (dotted lines). The H atoms not involved in relevant interactions are omitted for clarity.

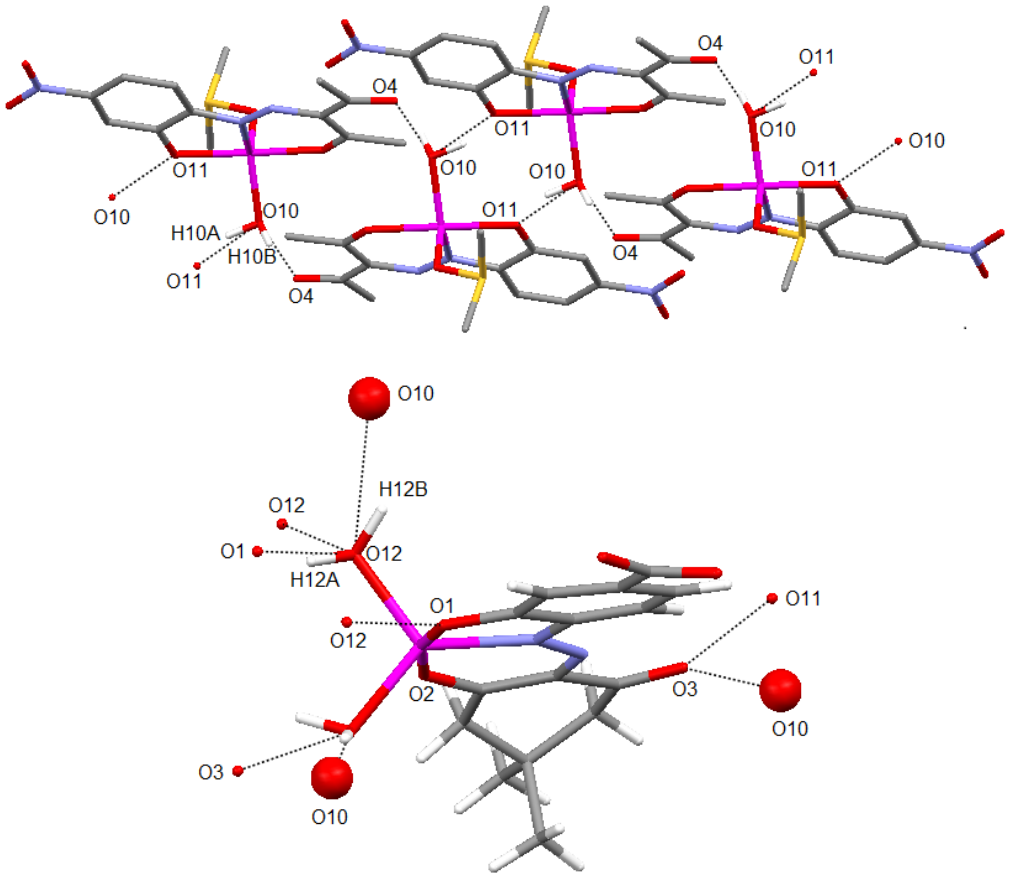


Figure S2. Structural representation of **6** (top) and **8** (down) showing the intermolecular H-bonds (dotted lines), which generate 1D chains (**6**) or, also with the aid of crystallization water molecules (shown as red ball), a 3D network (**8**). The H atoms, apart from those involved in H-bonds, are omitted for clarity.

Thermodynamics of interaction of zinc(II) nitrate and ligand 2 in solution

pH-metric titration:

The apparatus, general conditions, and methods of calculation are the same as those given in previous works.[2,5] The following mixtures (i)–(iii) were prepared and titrated potentiometrically against standard 0.08 mol·L^{-1} NaOH in 60 % (v/v) ethanol-water mixture at 298 K:

(i) 5.00 mL 0.001 M HCl + 5.00 mL 1.00 M KCl + 30.0 mL ethanol;

(ii) 5.00 mL 0.001 M HCl + 5.00 mL 1 M KCl + 25.0 mL ethanol + 5.00 mL 0.020 M ligand;

(iii) 5.00 mL 0.001 M HCl + 5.00 mL 1 M KCl + 25.0 mL ethanol + 5.00 mL 0.020 M ligand + 5.00 mL 0.020 M zinc salt.

For each mixture, the volume was made up to 50.0 mL with bidistilled water before the titration process. These titrations were also repeated at temperatures of 308 and 318 K.

Calculation of the stability constant (logk) of the Zn(II)-L^2 complex formation by the Martell-Chaberek method:[8a]

To determine the stability constant, the following relationships were used:[8a]

$$[L^{2-}] = \frac{(2-a)c_{H_2L} - [H^+] + [OH^-]}{[H^+]K_1^I + 2[H^+]^2 K_1^I K_2^I}, \qquad \alpha_{L(H)} = 1 + [H^+]K_1^I + [H^+]^2 K_1^I K_2^I,$$

$$k = \frac{c_{H_2L} - [L^{2-}]\alpha_{L(H)}}{[L^{2-}]^2 \alpha_{L(H)}}$$

where $c_{Zn} = 2.00 \times 10^{-3}$ M, $c_{H_2L} = 2.00 \times 10^{-3}$ M, K_1^I and K_2^I are the protonation constants of L^{2-} and HL^- ($K_1^I = 1/K_2$ and $K_2^I = 1/K_1$) and a is the neutralization point.

Dissociation constants:[2a]

$pK_1 = 6.35 \Rightarrow K_1 = 4.47 \cdot 10^{-7}$ M and $pK_2 = 10.22 \Rightarrow K_2 = 6.03 \cdot 10^{-11}$ M.

Protonation constants:

$K_1^1 = 1/K_2 = 1/6.03 \cdot 10^{-11} = 1.66 \cdot 10^{10}$ M^{-1} and $K_2^1 = 1/K_1 = 1/4.47 \cdot 10^{7} = 2.23 \cdot 10^{6}$ M^{-1}.

We titrated 50.0 mL of a solution with $2.00 \cdot 10^{-3}$ M of H_2L and $2.00 \cdot 10^{-3}$ M of Zn^{2+}, with a $8.00 \cdot 10^{-2}$ M solution of NaOH.

i) After addition of 0.50 mL of $8.00 \cdot 10^{-2}$ M solution of NaOH to 50.0 mL of $2.00 \cdot 10^{-3}$ M solution of Zn^{2+}+H_2L, we observed that pH 4.54 $\Rightarrow$ $[H^+] = 3.47 \cdot 10^{-5}$ and $[OH^-] = 2.88 \cdot 10^{-10}$ M.

Total concentration of NaOH:

0.50 mL $8.00 \cdot 10^{-2}$ M = 50.5 mL x_1 M $\Rightarrow$ $x_1 = 7.92 \cdot 10^{-4}$ M.

Total concentration of Zn^{2+}+H_2L:

50.0 mL $2.00 \cdot 10^{-3}$ M = 50.5 mL x_2 M $\Rightarrow$ $x_2 = 1.98 \cdot 10^{-3}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{7.92 \cdot 10^{-4}}{1.98 \cdot 10^{-3}} = 0.40$

$$[L^{2-}] = \{(2-a)c_{H_2L} - [H^+] + [OH^-]\} / \{[H^+]K_1^I + 2[H^+]^2 K_1^I K_2^I\} =$$

$$= \frac{\{(2-0.4) \cdot 2 \cdot 10^{-3} - 3.47 \cdot 10^{-5} + 2.88 \cdot 10^{-10}\}}{3.47 \cdot 10^{-5} \cdot 1.66 \cdot 10^{10} + 2(3.47 \cdot 10^{-5})^2 1.66 \cdot 10^{10} \cdot 2.23 \cdot 10^{6}} = 3.53 \cdot 10^{-11} \text{M}.$$

$$\alpha_{L(H)} = 1 + [H^+]K_1^1 + [H^+]^2 K_1^1 K_2^1 = 1 + 3.47 \cdot 10^{-5} \cdot 1.66 \cdot 10^{10} + (3.47 \cdot 10^{-5})^2 \cdot 1.66 \cdot 10^{10} \cdot 2.23 \cdot 10^{6} = 4.50 \cdot 10^{7}$$

$$k = \frac{2.00 \cdot 10^{-3} - 3.53 \cdot 10^{-11} \cdot 4.50 \cdot 10^{7}}{(3.53 \cdot 10^{-11})^2 \cdot 4.50 \cdot 10^{7}} = 7.24 \cdot 10^{9} \Rightarrow \log k = 9.86 .$$

(See Table S3).

ii) After addition of 1.00 mL of $8.00\cdot10^{-2}$ M solution of NaOH to 50.0 mL of $2.00\cdot10^{-3}$ M solution of Zn^{2+}+H_2L we observed that pH 4.73 $\Rightarrow$ $[H^+] = 1.86\cdot10^{-5}$ and $[OH^-] = 5.37\cdot10^{-10}$ M.

Total concentration of NaOH:

1.00 mL $8.00\cdot10^{-2}$ M = 51.0 mL x_1 M $\Rightarrow$ $x_1 = 1.57\cdot10^{-3}$ M.

Total concentration of Zn^{2+}+H_2L:

50.0 mL $2.00\cdot10^{-3}$ M = 51.0 mL x_2 M $\Rightarrow$ $x_2 = 1.96\cdot10^{-3}$ M.

Neutralization point: $a = \frac{x_1}{x_2} = \frac{1.57\cdot10^{-3}}{1.96\cdot10^{-3}} = 0.80$

$$[L^{2-}] = \{(2-a)c_{H_2L} - [H^+] + [OH^-]\}/\{[H^+]K_1^I + 2[H^+]^2 K_1^I K_2^I\} =$$

$$= \frac{\{(2-0.8)\cdot2\cdot10^{-3} - 1.86\cdot10^{-5} + 5.37\cdot10^{-10}\}}{1.86\cdot10^{-5}\cdot1.66\cdot10^{10} + 2(1.86\cdot10^{-5})^2 1.66\cdot10^{10}\cdot2.23\cdot10^{6}} = 9.19\cdot10^{-11}\text{M}.$$

$$\alpha_{L(H)} = 1 + [H^+]K_1^I + [H^+]^2 K_1^I K_2^I = 1 + 1.86\cdot10^{-5}\cdot1.66\cdot10^{10} + (1.86\cdot10^{-5})^2\cdot1.66\cdot10^{10}\cdot2.23\cdot10^{6} = 1.31\cdot10^{7}$$

$$k = \frac{2.00\cdot10^{-3} - 9.19\cdot10^{-11}\cdot1.31\cdot10^{7}}{(9.19\cdot10^{-11})^2\cdot1.31\cdot10^{7}} = 7.24\cdot10^{9} \Rightarrow \log k = 9.86.$$

(See Table S3).

iii) etc.

Table S3. Calculation of the stability constant of the zinc(II) complex with L^2 at 25 °C, in aqueous ethanol solution.

V_{KOH}, mL	a	pH	$[H^+]$, M	$[OH^-]$, M	$[L^{2-}]$, M	$\alpha_{L(H)}$	log$k$
0.50	0.40	4.54	$3.47\cdot10^{-5}$	$2.88\cdot10^{-10}$	$3.53\cdot10^{-11}$	$4.50\cdot10^{7}$	9.86
1.00	0.80	4.73	$1.86\cdot10^{-5}$	$5.38\cdot10^{-10}$	$9.19\cdot10^{-11}$	$1.31\cdot10^{7}$	9.86
1.50	1.20	5.01	$9.77\cdot10^{-6}$	$1.02\cdot10^{-9}$	$2.20\cdot10^{-10}$	$3.69\cdot10^{6}$	9.82
2.00	1.60	5.34	$4.57\cdot10^{-6}$	$2.19\cdot10^{-9}$	$4.91\cdot10^{-10}$	$8.49\cdot10^{5}$	9.89
2.50	2.00	5.69	$2.04\cdot10^{-6}$	$4.90\cdot10^{-9}$	–	–	log$k$ = 9.86 ± 0.04

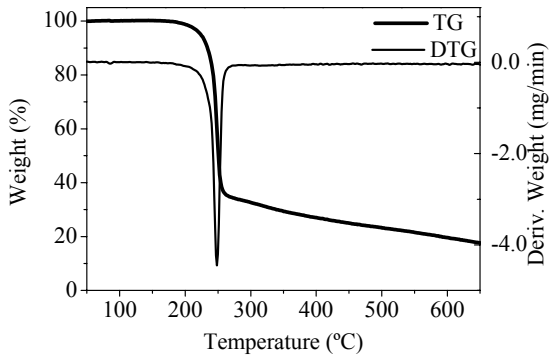
For determination of the thermodynamic functions of the complexation reaction, the following well known relationships were used:[8b]

$\Delta G^o = -2.303RT\log k$; $\Delta H^o = \{R(\log k_{(T_3)} - \log k_{(T_1)})\}/\{(1/T_3) - (1/T_1)\}$; $\Delta S^o = (\Delta H^o - \Delta G^o)/T$.

Table S4. Thermodynamic characteristics of the formation of the complex of Zn(II) with L^2 in aqueous ethanol solution.

T, K	log$k$	ΔG^o, kJ mol^{-1}	ΔH^o, kJ mol^{-1}	ΔS^o, J mol^{-1}K^{-1}
298±0.5	9.86±0.04	−56.26±0.14		82.05±1.82
308±0.5	9.68±0.02		−31.81±1.68	
318±0.5	9.51±0.06			

Thermal decomposition of 1−8



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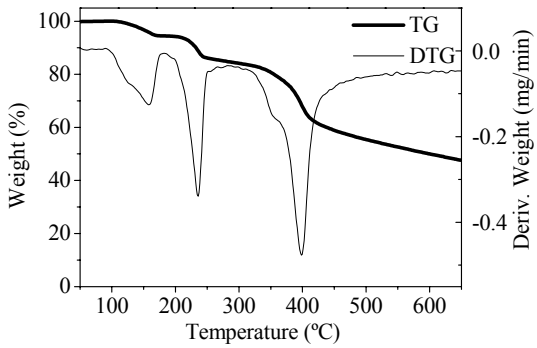

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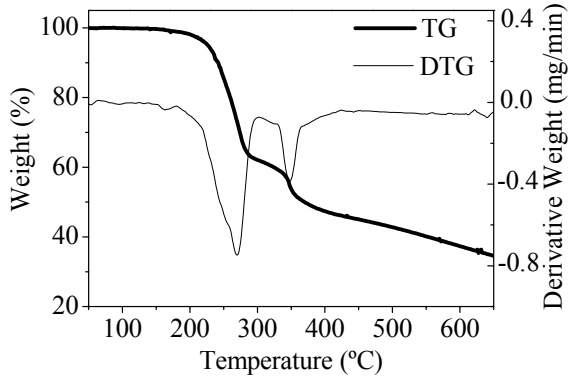

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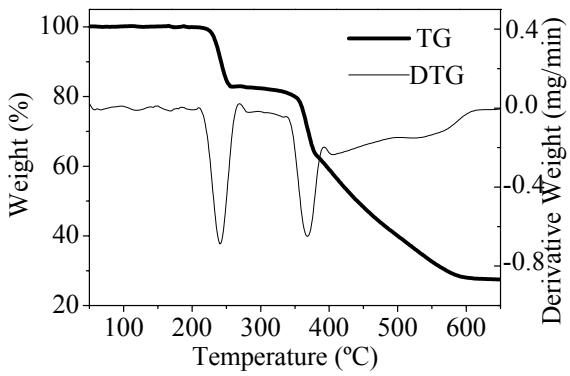

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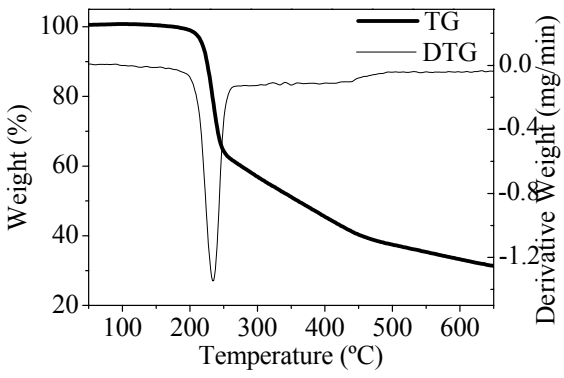

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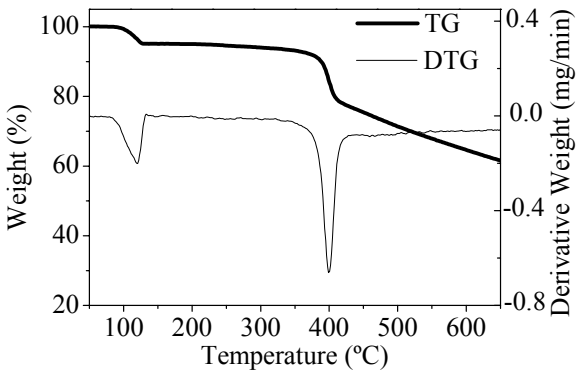

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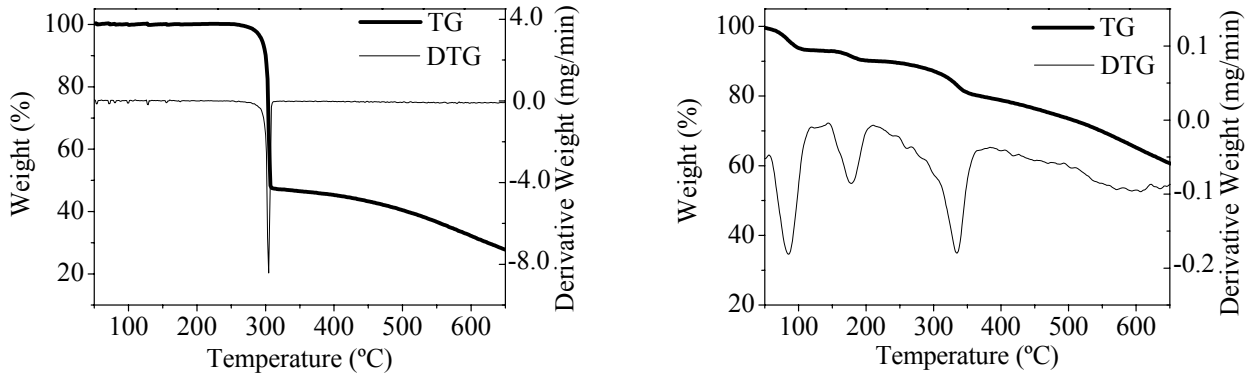


Figure S3. TG and DTG curves of **1**−**8**.

Table S5. Thermal behaviour of **1**−**8**.

Compound	Temperature range, °C	Weight loss, %	DTG peak temperature (°C)
1	211−292	65	254
2	194−277	31	233
	294−320	8.0	306
3	201−258	36	232
4	294−320	50	307
5	91−130	2.0	112
	204−235	7.0	213
	333−415	20	348
6	223−259	15	244
	345−384	17	370
7	87−133	5.0	123
	388−427	13	399
8	61−116	6.0	88
	137−213	3.0	168
	213−384	10	332

Catalytic studies

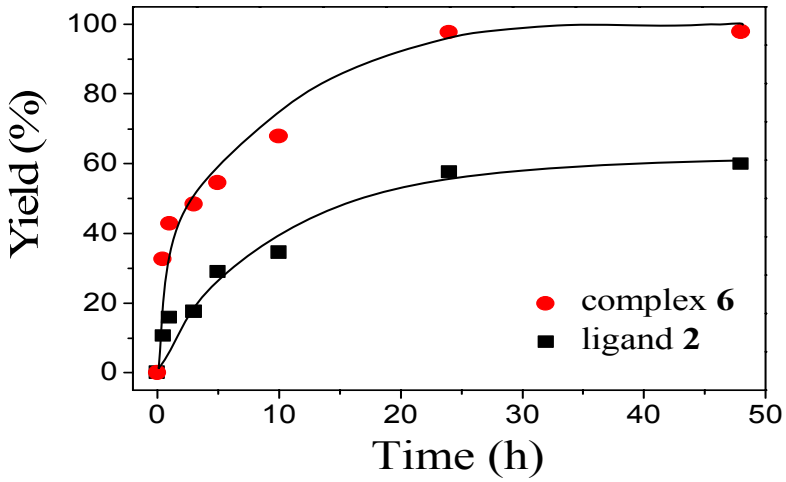


Figure S4. Accumulation of β-nitroalkanol (along the initial 48 h) in the Henry reaction of benzaldehyde and nitroethane, catalyzed by complex **6** (●) and ligand **2** (■).

Table S6. Variation of benzaldehyde concentration with time

Time, h	1	3	5	10	24
[benzaldehyde], mol L^{-1}	0.57	0.52	0.45	0.32	0.2
ln[benzaldehyde], mol L^{-1}	-0.56	-0.65	-0.80	-1.14	-1.61

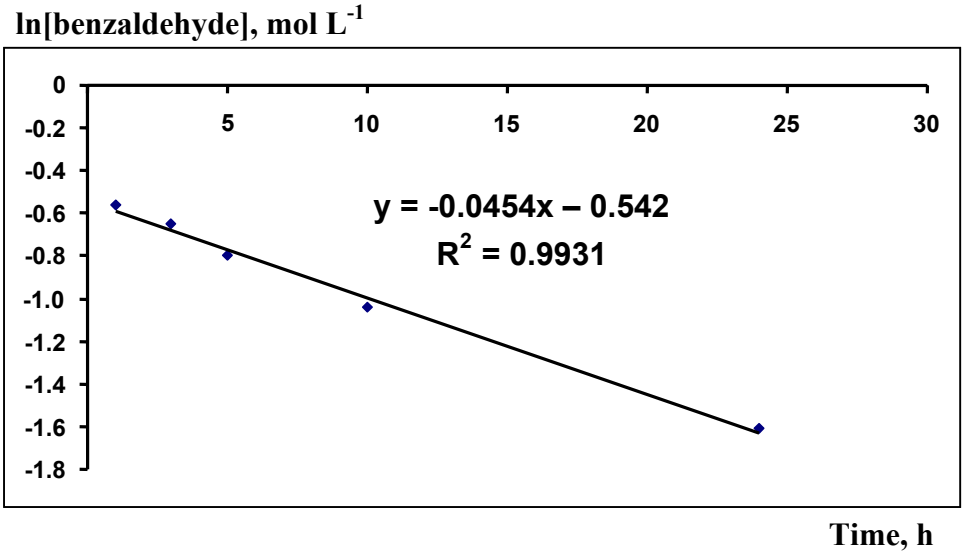


Figure S5. Plot of ln[benzaldehyde] *vs.* time.

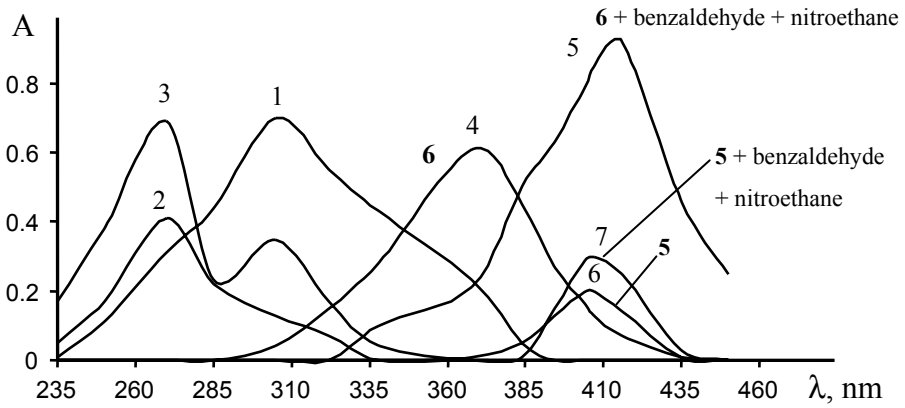


Figure S6. UV-vis spectra of starting materials and products for the Henry reaction: benzaldehyde (1), nitroethane (2), benzaldehyde + nitroethane (3), **6** (4), benzaldehyde + nitroethane + **6** (5), **5** (6), benzaldehyde + nitroethane + **5** (7); [benzaldehyde] = [nitroethane] = $4.00 \cdot 10^{-3}$ M, [**5**] = [**6**] = $1.00 \cdot 10^{-5}$ M in methanol.

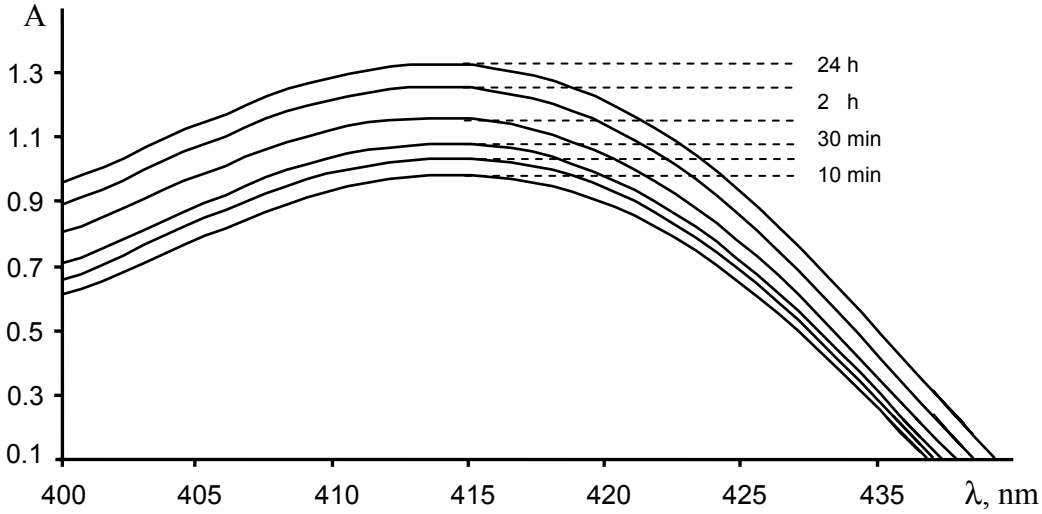


Figure S7. UV-vis monitoring of Henry reaction: [benzaldehyde] = [nitroethane] = $4.00 \cdot 10^{-3}$ M; [**6**] = $1.00 \cdot 10^{-5}$ M in methanol.

Calculation of the yield and selectivity for complex 6 in the Henry reaction

Total amount of compounds (see Fig. S7):

Bezaldehyde + *erythro* + *threo* = 0.23 + 2.26 + 7.28 = 9.77

Percentage of the unreacted bezaldehyde:

9.77 ---------- 100 %
0.23 ----------x } ⇒ x = 2.4 %

Conversion of benzaldehyde = yield of β-nitroalkanols = 100 – 2.4 = 97.6 %.

Yield of *erythro*:

9.77 ---------- 100 %
2.26 ----------x } ⇒ x = 23.1 %

Yield of *threo*:

9.77 ---------- 100 %
7.28 ----------x } ⇒ x = 74.5 %.

See Table 1, Entry 9.

***Selectivity*:**

Sum of *erythro* + *threo* = 23.1 + 74.5 = 97.6.

Selectivity of *erythro*:

97.6 ---------- 100 %
23.1 ----------x } ⇒ x = 24 %.

Selectivity of *threo*:

97.6 ---------- 100 %
74.5 ----------x } ⇒ x = 76 %.

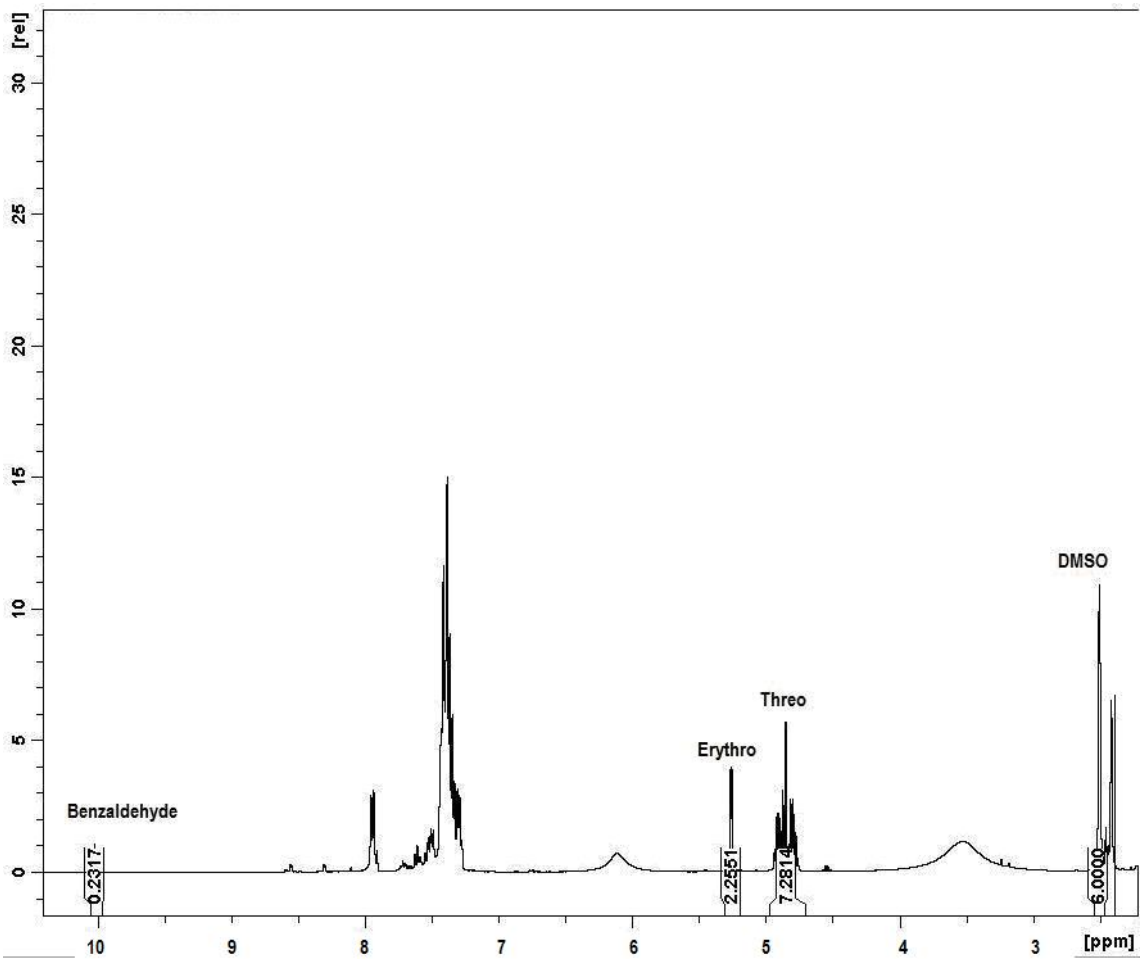
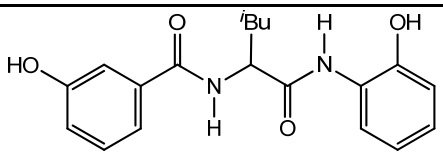
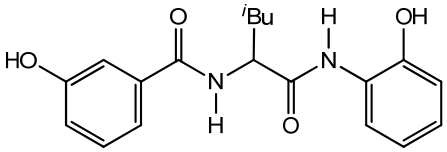
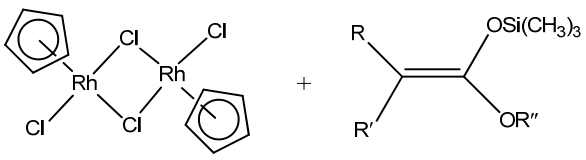
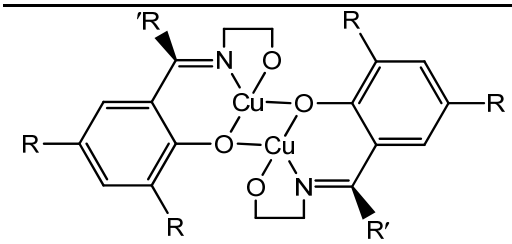


Figure S8. Example of integration in the ^{1}H NMR spectrum for the determination of Henry reaction products (Table 1, Entry 9).

Table S7. Compositon of some catalysts from Table 2

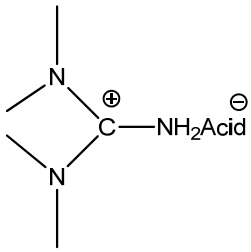
	Reference
$La(O^{i}Pr)_3 + NaN[Si(CH_3)_3]_2$ + 	6f
Lanthanum ($La(O^{i}Pr)_3$)/sodium source/amide ligand heterobimetallic catalyst	
$Nd(O^{i}Pr)_3 + NaN[Si(CH_3)_3]_2$ + 	6f
Neodymium ($Nd(O^{i}Pr)_3$)/sodium source/amide ligand heterobimetallic catalyst	
	6g
Rh complex in the presence of a silyl ketene acetal	

7n



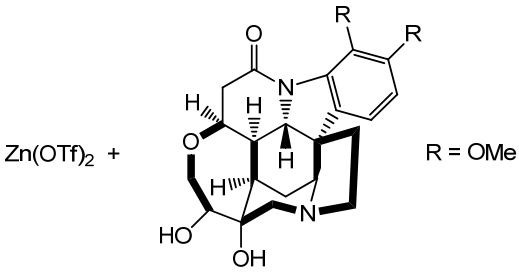
Chiral binuclear Cu(II) Schiff base complexes

7o



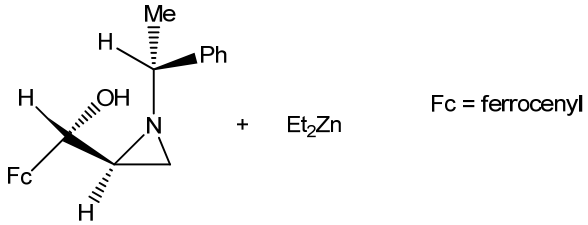
1,1,3,3-tetramethyl guanidine (TMG)-based ionic liquid

7m



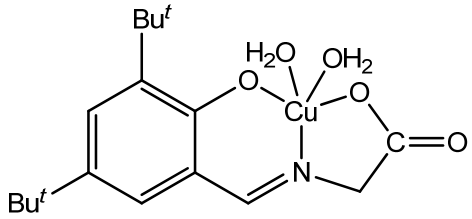
Zn Brucine-derived aminoalcohol

7p



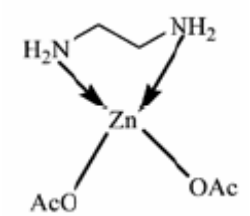
Ferrocenyl-substituted aziridinylmethanol (Fam) as a catalyst with Zn

7c



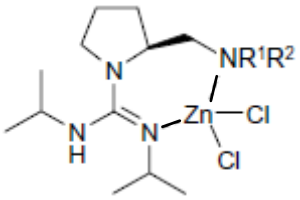
Phenoxide substituted Cu complex

7r



Mono ethylenediamine Zn complex

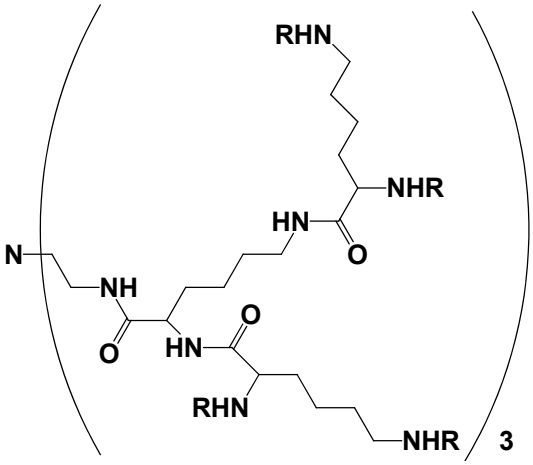
7s



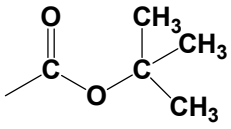
$R^1R^2 = (CH_2)_4$
$R^1R^2 = (CH_2)_2O(CH_2)_2$
$R^1R^2 = (CH_2)_5$

Zn(II) complexes with chiral guanidine ligands

7t



R =



Tertiary amines dendritically encapsulated within a flexible peptidic shell