

## Electronic Supporting Information

# Utilizing Tautomerization of 2-Amino-Oxazoline in Hydrogen Bonding Tripodal Ligands

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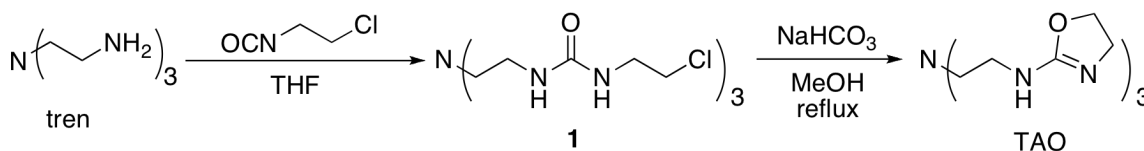
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## General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer. The synthesis of ligands and its intermediates were carried out under a dinitrogen atmosphere. The syntheses of metal complexes were conducted in a Vacuum Atmospheres, Co. drybox under an argon atmosphere. 1-tert-Butyl-3-(2-chloroethyl)urea (**2**) were prepared according to literature methods.<sup>1</sup> Electronic absorbance spectra were recorded with a Cary 50 spectrophotometer using a 1.00 mm quartz cuvette. Fourier transform infrared spectra were collected on a Varian 800 Scimitar Series FTIR spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX500 spectrometer. Magnetic moment of [Fe<sup>II</sup>TAO( $\kappa^1$ -SO<sub>4</sub>)] was measured by Evans method using DRX500 spectrometer.<sup>2</sup>

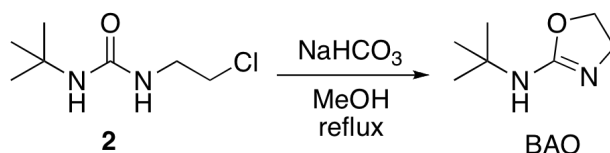
## Ligands Synthesis



**Preparation of 1,1',1''-(2,2',2''-nitriлотris(ethane-2,1-diyl))tris(3-(2-chloroethyl)urea) (1).** To a 500 mL round-bottom flask containing tren (1.0 g, 6.8 mmol) in THF (100 mL), 1-chloro-2-

isocyanatoethane (2.16 g, 20.5 mmol) dissolved in THF (100 mL) was added via dropwise at room temperature over 1 h. Between 30 min to 1 h later, an opaque gel-like solid began to form and the amount of solid increased over time. After allowing the reaction mixture to stirred overnight, diethyl ether (100 mL) was added to make the reaction mixture flow easily and the resulting gel-like solid was collected on glass frit, washed with more diethyl ether (50 mL) and dried under reduced pressure. The resulting white solid was used in the next step without further purification. Yield: 87-91%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, ppm): 2.41 (br t, 6H), 3.02 (br q, 6H), 3.31 (q, 6H), 3.54 (t, 6H), 6.06 (br t, 3H, urea NH), 6.28 (br t, 3H, urea NH). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, ppm): 157.5, 54.8, 44.4, 41.3, 37.4. FTIR (KBr disc, cm<sup>-1</sup>, selected bands): 3322, 3067, 3026, 2954, 2825, 1701, 1559, 1384, 1250. HRMS (ES<sup>+</sup>): Exact mass calcd for C<sub>15</sub>H<sub>30</sub>N<sub>7</sub>O<sub>3</sub>Cl [M + H], 462.1554. Found 462.1545.

**Preparation of *N*<sup>1</sup>-(4,5-dihydrooxazol-2-yl)-*N*<sup>2</sup>,*N*<sup>2</sup>-bis(2-(4,5-dihydrooxazol-2-ylamino)ethyl)ethane-1,2-diamine (TAO).** Compound **1** (2.9 g, 6.2 mmol) and NaHCO<sub>3</sub> (3.2 g, 37 mmol) were suspended in MeOH (100 mL) and refluxed at 90°C (silicon oil bath) overnight. The mixture initially became clear (2-3 h) but then a white precipitate began to form. After the reaction was completed, the precipitate was isolated via filtration and the filtrate was evaporated to afford syrup-like residue. The residue was suspended in CHCl<sub>3</sub> (100 mL) and refluxed for 1 h to extract the product from the residue. After cooling to room temperature, the resulting solution containing a white precipitate was passed through a Celite pad. The colorless or pale yellow filtrate was evaporated under reduced pressure and further dried *in vacuo* to afford 1.8 g of TAO (82%) as highly viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): 2.54 (t, 6H), 3.17 (t, 6H), 3.71 (t, 6H), 4.18 (t, 6H), 5.7 (br s, 3H, NH), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): 41.4, 52.5, 54.7, 67.9, 162.2 (imino C). FTIR (neat on NaCl disc, cm<sup>-1</sup>, selected bands) 3238 (N-H), 3055, 2948, 2815, 1657, 1548, 1479, 1351, 1326, 1257, 1172, 1031, 1000, 961, 930, 718. HRMS (ES<sup>+</sup>): Exact mass calcd for C<sub>15</sub>H<sub>27</sub>N<sub>7</sub>O<sub>3</sub> [M + H], 354.2254. Found 354.2258. For long-term storage, TAO should be redissolved in a proper solvent (e.g. MeOH, DCM or chloroform) and stored in that state for a later use. Otherwise, the dry TAO eventually becomes an insoluble transparent gel over 1 to 7 d. The time period for this process appears to depend on the degree of drying. Ring opening polymerization of oxazoline group might be one of the possible explanations for this effect.



**Preparation of *N*-tert-butyl-4,5-dihydrooxazol-2-amine (BAO).** Following a similar protocol used for the preparation of TAO, reaction between **2** (2.00 g, 11.2 mmol) and NaHCO<sub>3</sub> (2.8 g, 34 mmol) gave 1.35 g (84%) of BAO as a white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): 1.33 (s, 9H), 3.78 (t, 2H), 4.15 (t, 2H), 4.37 (br s, 1H, NH), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): 29.3, 51.0, 53.1, 66.8, 159.7 (imino C). FTIR (KBr disc, cm<sup>-1</sup>, selected bands) 3307 (N-H), 3181, 3079, 2971, 1752, 1677, 1636, 1556, 1481, 1453, 1363, 1282, 1217, 1066, 1037, 943, 771, 717. HRMS (ES<sup>+</sup>): Exact mass calcd for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O [M + H], 143.1184. Found 143.1180.

## Complex Synthesis

**Preparation of [Zn<sup>II</sup>BAO(*κ*<sup>1</sup>-OAc)<sub>2</sub>].** *N*-tert-butyl-4,5-dihydrooxazol-2-amine (101 mg, 0.710 mmol) and Zn(OAc)<sub>2</sub> (64.9 mg, 0.354 mmol) were dissolved in 4 mL of dry MeOH. After

stirring 1 h, the solvent was removed *in vacuo*. Minimal pentane was added to the residue and the mixture was allowed to stir for 1 h, after which the solvent was decanted and the solid dried once more under vacuum. The residue was then dissolved in 3 mL of Et<sub>2</sub>O, added to a test tube, and allowed to slowly evaporate. Large off-white crystals formed over the 5 d, yielding 122 mg (74%) crystalline product. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): 8.15 (2H, s, NH), 4.41 (4H, t, *J* = 8.6 Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.79 (4H, t, *J* = 8.6 Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 2.03 (6H, s, CH<sub>3</sub>COO<sup>-</sup>), 1.30 (18H, s, (CH<sub>3</sub>)<sub>3</sub>C), <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): 178.8 (CH<sub>3</sub>COO<sup>-</sup>), 164.6 (C<sub>ox</sub>), 69.0 (OCH<sub>2</sub>CH<sub>2</sub>N), 51.8 (OCH<sub>2</sub>CH<sub>2</sub>N), 49.1 ((CH<sub>3</sub>)<sub>3</sub>C), 29.7 ((CH<sub>3</sub>)<sub>3</sub>C), 23.5 (CH<sub>3</sub>COO<sup>-</sup>). Elemental analysis calcd for C<sub>18</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>Zn: C, 46.21; H, 7.32; N, 11.97%, found C, 46.09; H, 7.57; N, 11.93%. FTIR (KBr disc, cm<sup>-1</sup>, selected bands) 3315, 3205, 2974, 1658, 1395, 1083.

**Preparation of [Zn<sup>II</sup>TAO(κ<sup>1</sup>-OAc)(BPh<sub>4</sub>)].** To a solution of TAO (120 mg, 0.340 mmol) dissolved in 4 mL of dry MeOH was added Zn(OAc)<sub>2</sub> (60.7 mg, 0.331 mmol). The solution stirred for 1 h, after which NaBPh<sub>4</sub> (120. mg, 0.351 mmol) in 2 mL of MeOH was added, causing the immediate formation of a white precipitate. After stirring for 1 h, the mixture was filtered and the solid washed with MeOH and Et<sub>2</sub>O, then dried *in vacuo* to yield 225 mg (85%) of fine white powder. X-ray quality crystals were obtained from a propionitrile/ether diffusion mixture. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, ppm): [Zn(TAO)OAc]<sup>+</sup> 9.35 (2H, s, NH), 8.15 (1H, s, NH), 4.51 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>N), 4.37 (2H, t, *J* = 7.8 Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.58 (6H, m, OCH<sub>2</sub>CH<sub>2</sub>N), 3.18 (4H, m, N<sub>ap</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 3.05 (2H, t, *J* = 5.3 Hz, N<sub>ap</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 2.56 (6H, t, N<sub>ap</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 1.86 (3H, s, CH<sub>3</sub>COO<sup>-</sup>); BPh<sub>4</sub><sup>-</sup> 7.17 (8H, br t, *o*-Ar), 6.92 (8H, t, *J* = 7.3 Hz, *m*-Ar), 6.78 (4H, t, *J* = 7.2 Hz, *p*-Ar), <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, ppm) [Zn(TAO)OAc]<sup>+</sup> 177.68 (CH<sub>3</sub>COO<sup>-</sup>), 162.07 (N=C<sub>ox</sub>), 68.08 and 67.34 (OCH<sub>2</sub>CH<sub>2</sub>N), 51.99 and 51.66 (NCH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 43.50 and 41.57 (NCH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 41.76 (OCH<sub>2</sub>CH<sub>2</sub>N), 24.86 (CH<sub>3</sub>COO<sup>-</sup>); BPh<sub>4</sub><sup>-</sup> 163.27 (B-C1, *J*<sub>B-C</sub> = 195 Hz), 135.44 (C2), 125.29 (C3), and 121.51 (C4). Elemental analysis calcd for C<sub>41</sub>H<sub>50</sub>BN<sub>7</sub>O<sub>5</sub>Zn: C, 61.78; H, 6.32; N, 12.30%, found C, 61.53; H, 5.92; N, 12.17%. FTIR (KBr disc, cm<sup>-1</sup>, selected bands): 3191 (NH), 1692, 1663, 733, 704.

**Preparation of [Fe<sup>II</sup>TAO(κ<sup>1</sup>-SO<sub>4</sub>)].** To a solution of TAO (100. mg, 0.283 mmol) in 5 mL of MeOH was added FeSO<sub>4</sub>·7H<sub>2</sub>O (77 mg, 0.28 mmol) as a solid. The solution was initially colorless but after stirring for overnight became a pale green color. The reaction mixture was filtered through a medium glass frit to remove any insoluble materials and the product was precipitated by addition of diethyl ether (10 mL). The solid was collected on a glass frit, washed with diethyl ether and dried *in vacuo* to afford 103 mg (72%) of the product. Colorless crystals were obtained by layering diethyl ether over a MeOH solution of [Fe<sup>II</sup>TAO(κ<sup>1</sup>-SO<sub>4</sub>)]. Elemental analysis calcd for C<sub>15</sub>H<sub>29</sub>FeN<sub>7</sub>O<sub>7</sub>S: C, 35.51; H, 5.76; N, 19.33%, found: C, 35.72; H, 5.61; N, 19.04%. FTIR (KBr disc, cm<sup>-1</sup>, selected bands): 3331 (NH), 2953, 1669, 1111 (SO<sub>4</sub><sup>-</sup>), 605.  $\mu_{\text{eff}} = 5.03 \mu\text{B}$ .

**Preparation of [Zn<sup>II</sup>TAO(κ<sup>1</sup>-SO<sub>4</sub>)].** To a solution of TAO (105 mg, 0.298 mmol) dissolved in 5 mL of dry MeOH was added anhydrous ZnSO<sub>4</sub> (44.6 mg, 0.276 mmol). The cloudy mixture was allowed to stir for 4 h, after which the solution became clear. The solvent volume was reduced in volume to approximately 2.5 mL *in vacuo*, was added to a vial, and placed inside an ether diffusion chamber. X-ray suitable crystals formed after 5 d, which were washed with Et<sub>2</sub>O and dried to afford 104 mg (73%) of the off-white crystalline product. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta_{\text{H}}$  (ppm) 9.25 (3H, s, NH), 4.46 (6H, t, *J* = 7.8 Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.52 (6H, t, *J* = 7.9 Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.21 (6H, t, *J* = 5.5 Hz, N<sub>ap</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 2.55 (6H, t, N<sub>ap</sub>CH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>); <sup>13</sup>C NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta_{\text{C}}$  (ppm) 161.8 (N=C<sub>ox</sub>), 67.5 (OCH<sub>2</sub>CH<sub>2</sub>N), 51.0 (NCH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>), 42.2 (OCH<sub>2</sub>CH<sub>2</sub>N), 41.6 (NCH<sub>2</sub>CH<sub>2</sub>NC<sub>ox</sub>). Elemental analysis calcd for C<sub>15</sub>H<sub>27</sub>N<sub>7</sub>O<sub>7</sub>SZn: C, 34.99; H,

5.29; N, 19.04%, found: C, 35.23; H, 4.91; N, 18.63%. FTIR (KBr disc,  $\text{cm}^{-1}$ , selected bands): 3258 (NH), 2975, 2905, 1692 (CN), 1657, 1098 ( $\text{SO}_4^-$ ).

### Crystallography

**Structure of  $[\text{Zn}^{\text{II}}\text{BAO}(\kappa^1\text{-OAc})_2]$ .** A colorless crystal of approximate dimensions 0.16 x 0.28 x 0.34 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>3</sup> program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>4</sup> and SADABS<sup>5</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>6</sup> program. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P\bar{1}$  was assigned and later determined to be correct. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>7</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms, with the exception of those associated with C(18), were located from a difference-Fourier map and refined ( $x, y, z$  and  $U_{\text{iso}}$ ). Hydrogen atoms H(18A), H(18B) and H(18C) were included using a riding model. At convergence,  $wR2 = 0.0650$  and  $\text{Goof} = 1.046$  for 387 variables refined against 5256 data ( $0.76\text{\AA}$ ),  $R1 = 0.0237$  for those 4979 data with  $I > 2.0\sigma(I)$ .

**Structure of  $[\text{Zn}^{\text{II}}\text{TAO}(\kappa^1\text{-OAc})(\text{BPh}_4)]$ .** A colorless crystal of approximate dimensions 0.18 x 0.22 x 0.27 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>3</sup> program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>4</sup> and SADABS<sup>5</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>6</sup> program. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group  $P\bar{1}$  was assigned and later determined to be correct. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>7</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms H(5), H(6) and H(7) were located from a difference-Fourier map and refined ( $x, y, z$  and  $U_{\text{iso}}$ ). The remaining hydrogen atoms were included using a riding model. At convergence,  $wR2 = 0.0960$  and  $\text{Goof} = 1.051$  for 509 variables refined against 8701 data ( $0.77\text{\AA}$ ),  $R1 = 0.0350$  for those 7882 data with  $I > 2.0\sigma(I)$ .

**Structure of  $[\text{Fe}^{\text{II}}\text{TAO}(\kappa^1\text{-SO}_4)]$ .** A colorless crystal of approximate dimensions 0.17 x 0.18 x 0.26 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2<sup>3</sup> program package was used to determine the unit-cell parameters and for data collection (35 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT<sup>4</sup> and SADABS<sup>5</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>6</sup> program. The diffraction symmetry was  $mmm$  and the systematic absences were consistent with the orthorhombic space group  $P2_12_12_1$  that was later determined to be correct. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. The analytical scattering factors<sup>7</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined ( $x, y, z$  and  $U_{\text{iso}}$ ). At convergence,  $wR2 = 0.0589$  and  $\text{Goof} = 1.035$  for 388 variables refined against 4709 data ( $0.76\text{\AA}$ ),  $R1 = 0.0231$  for those 4464 data with  $I > 2.0\sigma(I)$ . The absolute structure was assigned by refinement of the Flack parameter<sup>8</sup>

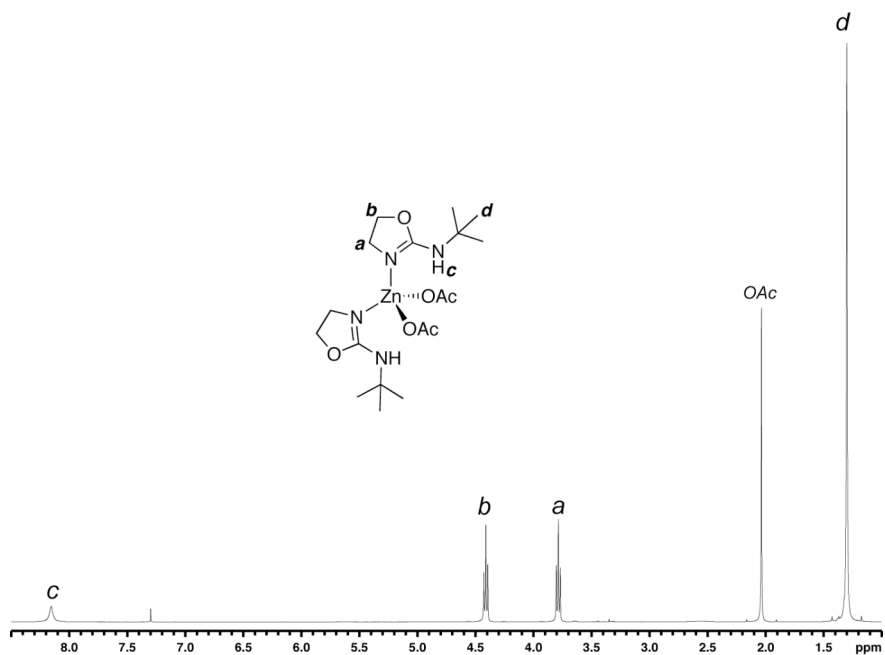
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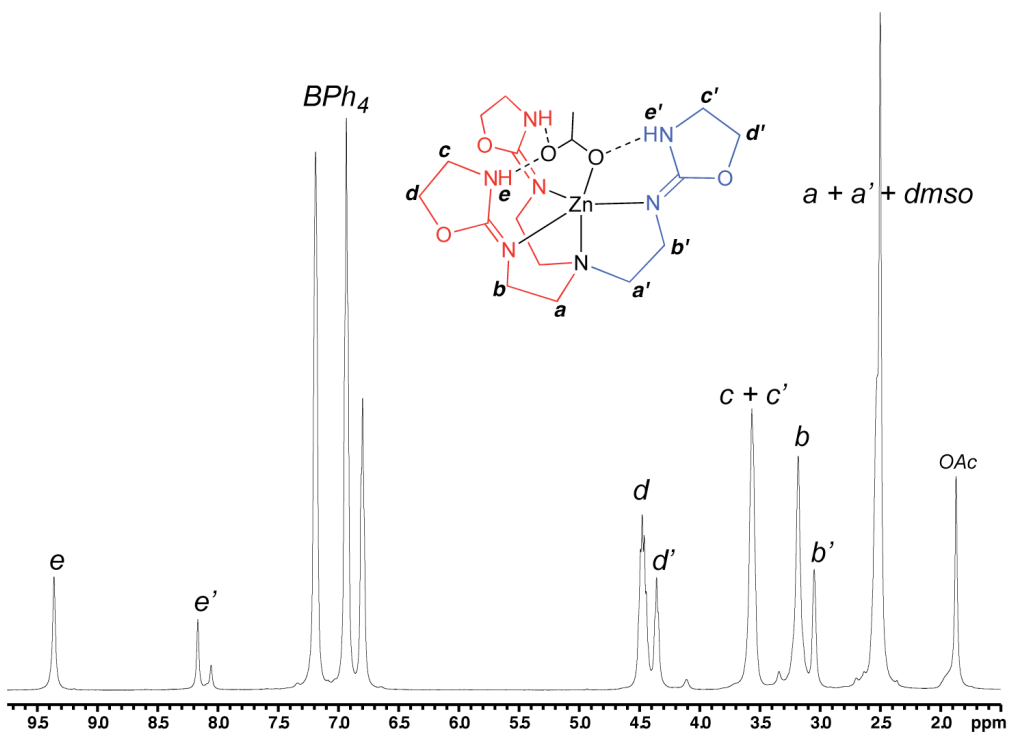
**Table S1.** Crystal data and structure refinements for  $[\text{Zn}^{\text{II}}\text{BAO}(\kappa^1\text{-OAc})_2]$ ,  $[\text{Zn}^{\text{II}}\text{TAO}(\kappa^1\text{-OAc})]$  (BPh<sub>4</sub>) and  $[\text{Fe}^{\text{II}}\text{TAO}(\kappa^1\text{-SO}_4)]$

Compound	$[\text{Zn}^{\text{II}}\text{BAO}(\kappa^1\text{-OAc})_2]$	$[\text{Zn}^{\text{II}}\text{TAO}(\kappa^1\text{-OAc})(\text{BPh}_4)]$	$[\text{Fe}^{\text{II}}\text{TAO}(\kappa^1\text{-SO}_4)]$
Empirical formula	C <sub>18</sub> H <sub>34</sub> N <sub>4</sub> O <sub>6</sub> Zn	C <sub>41</sub> H <sub>50</sub> B N <sub>7</sub> O <sub>5</sub> Zn	C <sub>15</sub> H <sub>27</sub> Fe N <sub>7</sub> O <sub>7</sub> S
Formula weight	467.86	797.06	505.35
Temperature	93(2) K	173(2) K	153(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	<i>P</i> 1-	<i>P</i> 1-	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>
Unit cell dimensions	a = 9.4007(4) Å α = 82.3476(4)°	a = 11.2142(5) Å α = 88.7516(5)°	a = 9.5480(10) Å α = 90°
	b = 9.6910(4) Å β = 72.3190(4)°	b = 12.9201(6) Å β = 76.4113(5)°	b = 14.2375(15) Å β = 90°
	c = 13.1099(5) Å γ = 87.6900(4)°	c = 14.3636(6) Å γ = 71.5359(5)°	c = 14.8769(15) Å γ = 90°
Volume	1127.79(8) Å <sup>3</sup>	1915.61(15) Å <sup>3</sup>	2022.4(4) Å <sup>3</sup>
Z	2	2	4
Density (calculated)	1.378 Mg/m <sup>3</sup>	1.382 Mg/m <sup>3</sup>	1.660 Mg/m <sup>3</sup>
Absorption coefficient	1.128 mm <sup>-1</sup>	0.696 mm <sup>-1</sup>	0.905 mm <sup>-1</sup>
F(000)	496	840	1056
Crystal color	colorless	colorless	colorless
Crystal size	0.34 x 0.28 x 0.16 mm <sup>3</sup>	0.27 x 0.22 x 0.18 mm <sup>3</sup>	0.26 x 0.18 x 0.17 mm <sup>3</sup>
Theta range for data collection	2.12 to 27.87°	1.97 to 27.50°	1.98 to 27.87°
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	-12 ≤ h ≤ 12, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	13329	22314	20954
Independent reflections	5256 [R(int) = 0.0158]	8701 [R(int) = 0.0204]	4709 [R(int) = 0.0231]
Completeness to theta	27.87° (97.8 %)	27.50° (98.7 %)	27.87° (98.9 %)
Absorption correction	Numerical	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8384 and 0.7030	0.8849 and 0.8343	0.8613 and 0.7987
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5256 / 0 / 387	8701 / 0 / 509	4709 / 0 / 388
Goodness-of-fit on F <sup>2</sup>	1.046	1.051	1.035
Final R indices	[I > 2σ(I) = 4979 data] R1 = 0.0237, wR2 = 0.0641	[I > 2σ(I) = 7882 data] R1 = 0.0350, wR2 = 0.0933	[I > 2σ(I) = 4464 data] R1 = 0.0231, wR2 = 0.0580
R indices (all data)	R1 = 0.0252, wR2 = 0.0650	R1 = 0.0389, wR2 = 0.0960	R1 = 0.0252, wR2 = 0.0589
Absolute structure parameter			0.011(12)
Largest diff. peak and hole	0.468 and -0.330 e.Å <sup>-3</sup>	0.837 and -0.493 e.Å <sup>-3</sup>	0.334 and -0.204 e.Å <sup>-3</sup>

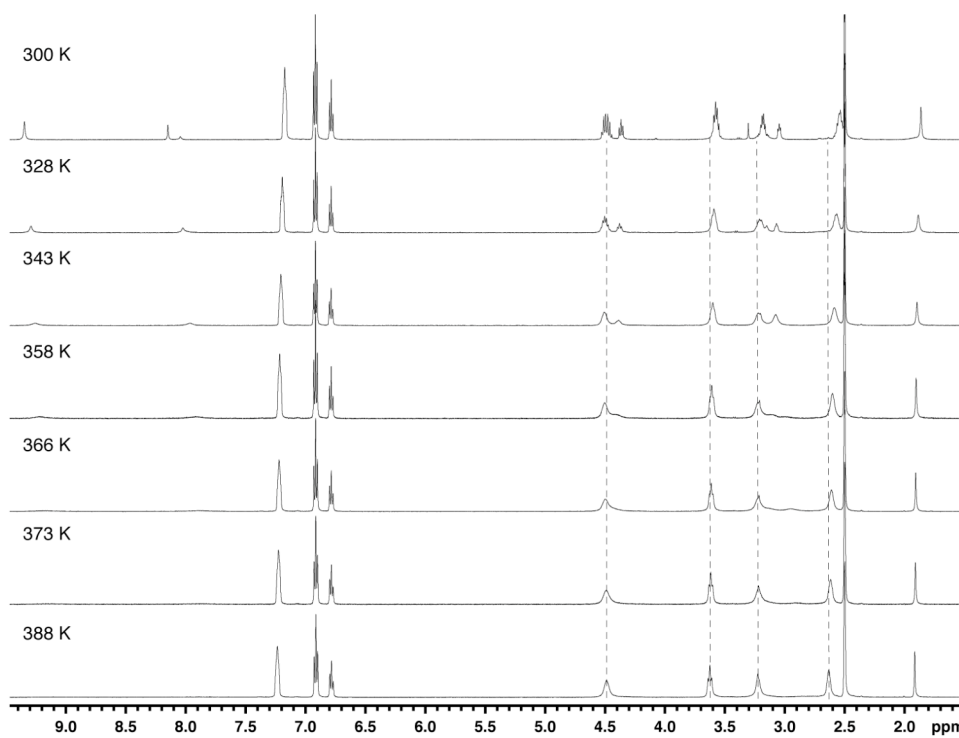
Definitions:  $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$ ,  $R1 = \sum||F_o| - |F_c|| / \sum|F_o|$ ,  $Goof = S = [\sum[w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$  where n is the number of reflections and p is the total number of parameters refined.



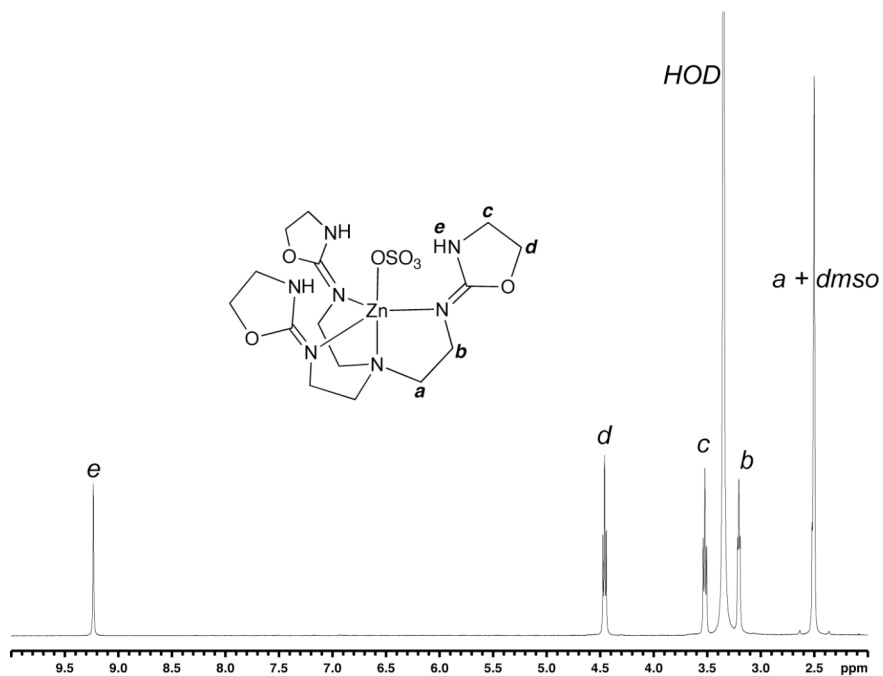
**Figure S1.** <sup>1</sup>H NMR spectrum of [Zn<sup>II</sup>BAO(κ<sup>1</sup>-OAc)<sub>2</sub>] in CDCl<sub>3</sub>.



**Figure S2.** <sup>1</sup>H NMR spectrum of [Zn<sup>II</sup>TAO(κ<sup>1</sup>-OAc)(BPh<sub>4</sub>)] in DMSO-d<sub>6</sub>.



**Figure S3.** Variable temperature <sup>1</sup>H NMR spectra of [Zn<sup>II</sup>TAO(κ<sup>1</sup>-OAc)(BPh<sub>4</sub>)] in DMSO-d<sub>6</sub>.



**Figure S4.** <sup>1</sup>H NMR spectrum of [Zn<sup>II</sup>TAO(κ<sup>1</sup>-SO<sub>4</sub>)] in DMSO-d<sub>6</sub>.