

Supplementary Material

for

Hydrosoluble complexes bearing tris(pyrazolyl)methane sulfonate ligand: synthesis, characterization and catalytic activity for Henry reaction

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Table S1. Crystallographic data and structure refinement details for Li(Tpms) and **1**.

| | Li(Tpms) | Compound 1 |
|---|---|---|
| Empirical formula | C ₂₀ H ₁₈ Li ₂ N ₁₂ O ₆ S ₂ | C ₂₀ H ₁₈ CuN ₁₂ O ₆ S ₂ |
| Formula Weight | 600.46 | 650.12 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | P 21/c | P b c a |
| Temperature/K | 296(2) | 296(2) |
| <i>a</i> /Å | 19.1190(3) | 13.6171(6) |
| <i>b</i> /Å | 8.4119(3) | 12.5657(5) |
| <i>c</i> /Å | 18.7067(6) | 14.1981(6) |
| α /° | 90 | 90 |
| β /° | 119.046(2) | 90 |
| γ /° | 90 | 90 |
| <i>V</i> (Å ³) | 2630.16(14) | 2429.41(18) |
| <i>Z</i> | 4 | 4 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.516 | 1.777 |
| <i>F</i> 000 | 1232 | 1324 |
| μ (Mo K α) (mm ⁻¹) | 0.265 | 1.139 |
| Rfls. collected/unique/observed | 20434/5400/2662 | 26583/4248/2908 |
| <i>R</i> _{int} | 0.1186 | 0.0583 |
| Final <i>R</i> 1 ^a , <i>wR</i> 2 ^b (<i>I</i> ≥ 2σ) | 0.0581, 0.1039 | 0.0373, 0.0834 |
| Goodness-of-fit on <i>F</i> ² | 0.919 | 1.022 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR(F^2) = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4]^{1/2}.$$

Table S2. Selected bond distances (Å) and angles (°) for Li(Tpms) and **1**.^a

| Li(Tpms) | | 1 | |
|---|----------|------------------------|------------|
| Li1-O1 ⁱ | 1.930(7) | Cu1-N1 | 1.9829(16) |
| Li1-N2 ⁱ | 2.039(7) | Cu1-N3 | 1.9898(16) |
| Li1-O3 | 1.917(7) | Cu1-O3 | 2.3480(16) |
| Li1-N4 | 2.049(8) | N1-Cu1-N3 | 86.28(7) |
| Li2-N12 ⁱⁱ | 2.028(7) | N3-Cu1-O3 | 86.18(6) |
| Li2-O5 ⁱⁱ | 1.929(8) | N1-Cu1-O3 | 83.32(7) |
| Li2-O6 | 1.942(6) | O3-Cu1-O3 ⁱ | 180.00 |
| Li2-N10 | 2.05(1) | N1-Cu1-N1 ⁱ | 180.00 |
| N2 ⁱ -Li1-O1 ⁱ | 93.3(3) | N3-Cu1-N3 ⁱ | 180.00 |
| N2 ⁱ -Li1-O3 | 123.8(4) | N3-Cu1-O3 ⁱ | 93.82(6) |
| O3-Li1-N4 | 95.3(3) | N1-Cu1-N3 ⁱ | 93.72(7) |
| N4-Li1-O1 ⁱ | 126.3(4) | N1-Cu1-O3 ⁱ | 96.68(7) |
| N12 ⁱⁱ -Li2-O5 ⁱⁱ | 95.1(3) | | |
| O6-Li2-O5 ⁱⁱ | 116.6(4) | | |
| O6-Li2-N10 | 93.6(3) | | |
| N10-Li2-N12 ⁱⁱ | 106.7(3) | | |

^a Symmetry codes for generating equivalent atoms: i) 1-x,1/2+y,1/2-z [Li(Tpms)] or -x,-y,1-z (**1**); ii) -x,1/2+y,1/2-z.

Structure of Li(Tpms)

Slow evaporation of a MeOH solution of Li(Tpms) at room temperature afforded colorless crystals of the compound, that were analyzed by SCXRD (Figure S1).

A molecular structure of this polymer has already been reported [1] where the crystals were obtained from MeCN solution. It crystallized in the orthorhombic space group $Pbc2_1$, the asymmetric unit contained an assembly formed by two Tpms ligands bound to two lithium cations, the symmetry expansion led to a 1D infinite chain spreading along the crystallographic b axis.

The Li(Tpms) of our study crystallized in the monoclinic space group $P2_1/c$, the asymmetric unit comprising two crystallographically independent Tpms ligands each one *NO*-coordinated to a lithium cation and leading, upon symmetry expansion, to two 1D chains one connecting Li1 and the other Li2, both along b (Figure S2). The metal centres join two six-membered Li–O–S–C–N–N cycles and display distorted N_2O_2 -tetrahedral environments as expressed by the $\tau_4[2]$ values of 0.76 and 0.77; ideally, they should be 1.00 for perfect tetrahedral settings. Expectedly, the sum of the six coordination bond angles in the structure deviate from the expected 720° for a perfect tetrahedron [3] and is given by 659.4° (for Li1) and 658.9° (for Li2). Such deviations are conceivably due to the severe strain conferred by the metallacycles with the internal O–Li–N bond angles (Table S2) considerably smaller [$93.3(3)$ – $95.3(3)^\circ$ range] than the other four [$106.7(3)$ – $126.3(4)^\circ$ range].

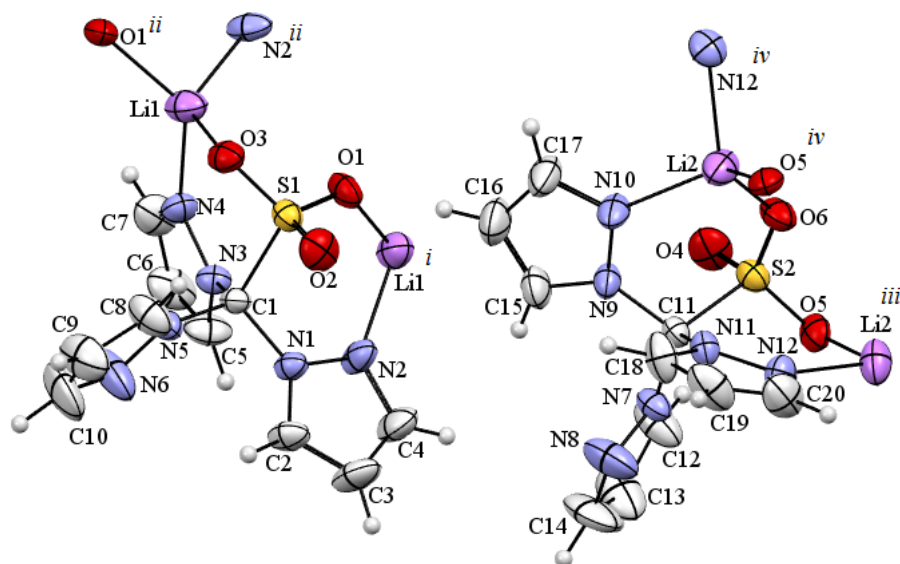


Figure S1. ORTEP diagram of Li(Tpms) with displacement ellipsoids drawn at 40% probability level and partial atom labelling scheme. Symmetry operations to generate the equivalent atoms: *i*) $1-x, -1/2+y, 1/2-z$; *ii*) $1-x, 1/2+y, 1/2-z$; *iii*) $-x, -1/2+y, 1/2-z$; *iv*) $-x, 1/2+y, 1/2-z$.

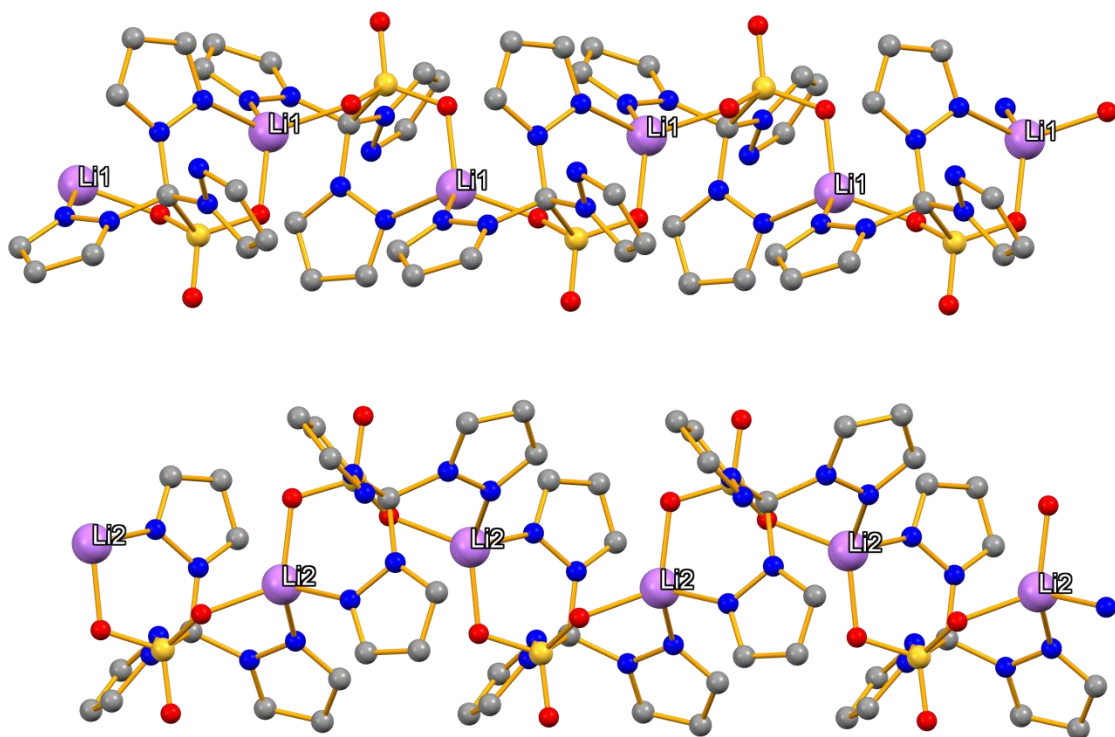


Figure S2. Structural fragment representing the two chains of the 1D polymer of Li(Tpms). Hydrogen atoms were omitted for clarity. Color codes: lithium (violet), sulfur (yellow), oxygen (red), nitrogen (blue) and carbon (gray).

Calculation of nitroaldol reaction yields using ^1H NMR analysis of crude products

A. For the reactions using nitromethane

The ^1H NMR spectrum of crude products from nitroaldol condensation of benzaldehyde with nitromethane under the conditions described at Table 1, entry 23, is displayed in Figure S3.

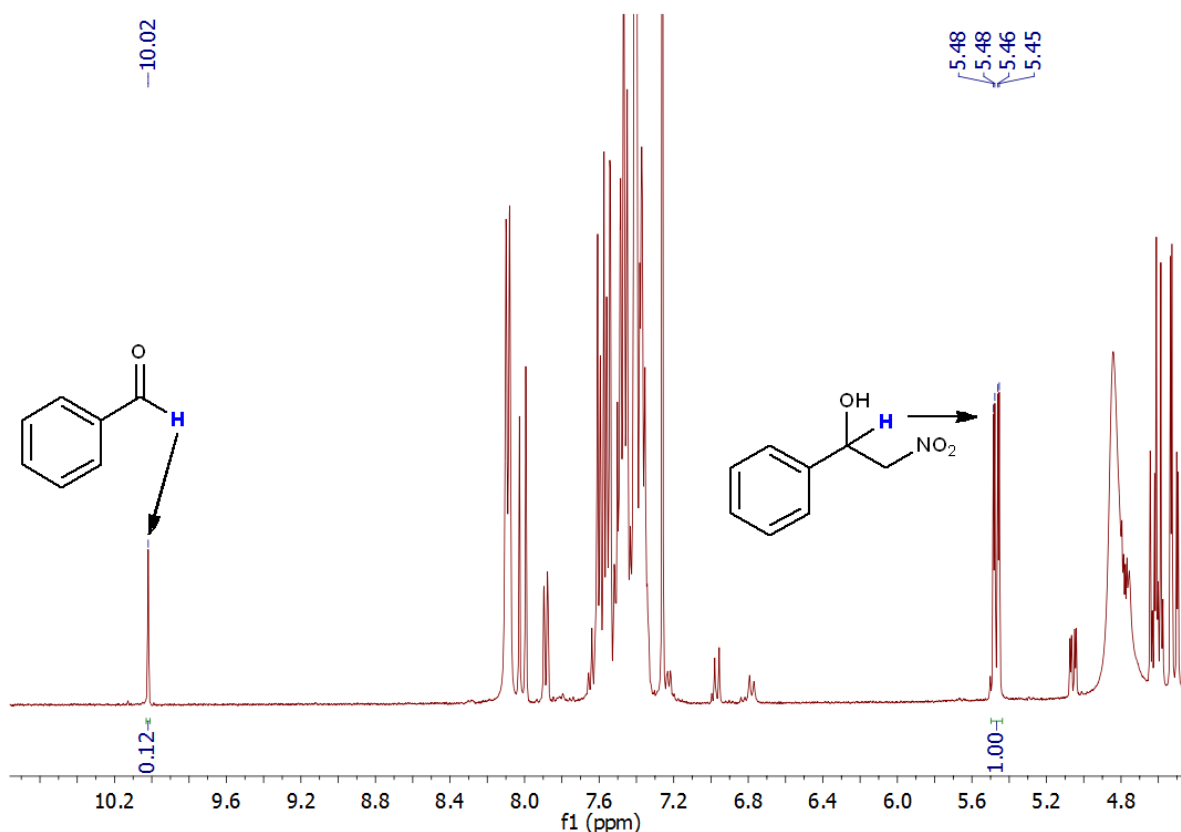


Figure S3. ^1H NMR spectrum (CDCl_3 ; 400 MHz) of crude product from nitroaldol condensation of benzaldehyde with nitromethane using 5 mol% of catalyst **1** (Table 1, entry 23).

The yield is calculated by dividing characteristic peak area of the corresponding product by sum of characteristic peak areas of substrate and corresponding product.

$$\text{Yield (\%)} = [a/(a + b)] \times 100\%$$

a: characteristic peak area of the corresponding product.

b: characteristic peak area of substrate.

Characteristic peak area of 1-phenyl-2-nitroethanol = 1

Characteristic peak area of benzaldehyde = 0.12

$$\text{Yield} = [1/(1+0.12)] \times 100 = \mathbf{89.3\%}$$

B. For the reactions using nitroethane

The ^1H NMR spectrum of crude products from nitroaldol condensation of benzaldehyde with nitroethane under the conditions described at Table 2, entry 2, is displayed in Figure S4.

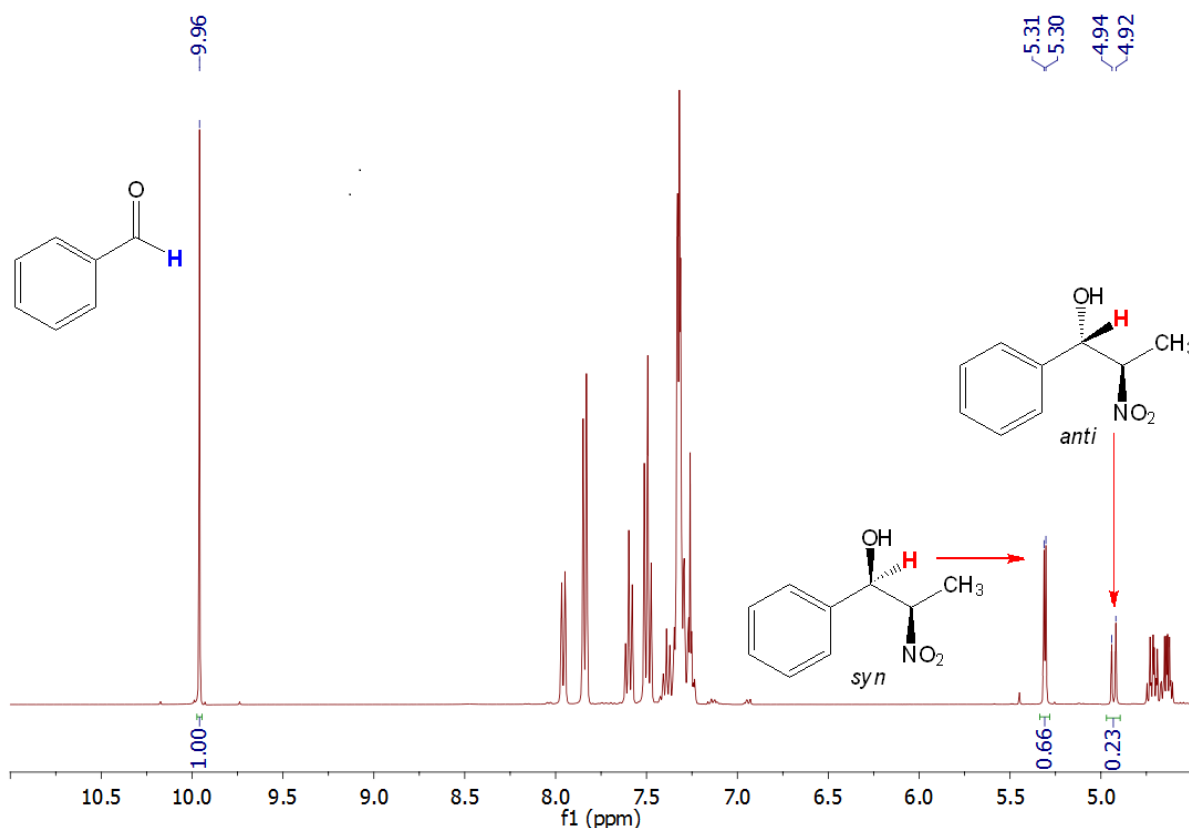


Figure S4. ^1H NMR spectrum (CDCl_3 ; 400 MHz) of crude product from nitroaldol condensation of benzaldehyde with nitroethane using 5 mol% of catalyst **1** (Table 2, entry 2).

The yield is calculated by dividing characteristic peak areas of the corresponding products (both *anti* and *syn*) by sum of characteristic peak areas of substrate and corresponding products.

$$\text{Yield (\%)} = [(a + b)/(a + b + c)] \times 100\%$$

a: characteristic peak area of the product in *anti*-form.

b: characteristic peak area of the product in *syn*-form.

c: characteristic peak area of substrate.

Ratio of the product in *anti* and *syn* forms is calculated by comparing between their characteristic peak areas.

Characteristic peak area of 1-phenyl-2-nitropropanol in “*anti*” form = 0.23

Characteristic peak area of the product in “*syn*” form = 0.66

Characteristic peak area of substrate = 1

Yield = $[(0.23 + 0.66) / (1 + 0.23 + 0.66)] \times 100 = 47.1 \%$

Product in "*anti*" form = $[0.23 / (0.23 + 0.66)] \times 100 = 25.8 \%$

Product in "*syn*" form = $[0.66 / (0.23 + 0.66)] \times 100 = 74.2 \%$

syn : *anti* = **74.2 : 25.8**

Table S3. Comparison of various catalytic systems for Henry reaction of benzaldehyde with nitroethane in aqueous medium.

| | Catalyst | Reaction Conditions | | Yield (%) | Selectivity (anti : syn) | Ref |
|----|--|---------------------|------------------|----------------|--------------------------|------------|
| | | Time (h) | Temperature (°C) | | | |
| 1 | Cu{κ ³ (<i>N,N',O</i>)-O ₃ SC(pz) ₃ } ₂ (1) | 48 | 100 | 85 | 75:25 | This Study |
| 2 | [Zn(DMSO)(H ₂ O)(L)] L = 3-(2-hydroxy-4-nitrophenylhydrazo)pentane-2,4-dione | 24 | 20 | 73 | 29:71 | [4] |
| 3 | [Cu ₂ (H ₂ O)(L) ₂] ₂ 2-(2-(dicyanomethylene)hydrazinyl)-benzoic acid | 24 | 23 | 89 | 29:71 | [5] |
| 4 | [Fe(H ₂ O) ₃ (L)] 5H ₂ O L = 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2-hydroxy-benzenesulfonic acid | 24 | 45 | 95 | 26:74 | [6] |
| 5 | [Ni ₂ (HL) ₂] 4MeOH HL = N ¹ ,N ³ -bis(2-hydroxybenzylidene)malonohydrazide | 24 | 60 | 93 | 72:28 | [7] |
| 6 | [KLa(L) ₂ (DMF) ₂ (H ₂ O) ₃] L = 3-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonate | 24 | 20 | 91 | 24:76 | [8] |
| 7 | [Sm(H ₂ O) ₉](L) ₃ 2H ₂ O L = (E,Z)-5-chloro-3-(2-(1,3-dioxo-1-phenylbutan-2-ylidene)hydrazinyl)-2-hydroxybenzenesulfonate | 24 | 20 | 78 | 25:75 | [8] |
| 8 | [UO ₂ (L1) ₂ (R)] [Ni(L1) ₂ (DMSO) ₂] L1 = 1,3-diphenyl-propane-1,3-dione | 24 | 20 | 33 41 | 42:58 39:61 | |
| 9 | [Co(H ₂ O) ₄ (L2) ₂] 2H ₂ O [UO ₂ (H ₂ O) ₂ (L2) ₂] 2H ₂ O L2 = 4-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl)benzoic acid | 24 | 75 20 | 90 55 | 31:69 27:73 | [9] |
| 10 | Zn[NH=C(CCl ₃)NC(CCl ₃)=NH] ₂ | 24 | 20 | 29 | 48:52 | [10] |
| 11 | [Zn ₂ (L) ₂ (4,4'-bipyridine) ₂ (H ₂ O)(DMF)] _n L = 2-acetamidoterephthalate | 48 | 70 | 78 | 80:20 | [11] |
| 12 | [Cu(L)(H ₂ O) ₄] L = 2-propionamidoterephthalate | 30 | 70 | 77 | 82:18 | |
| 13 | [Cu(L)(H ₂ O) ₄] L = 2-acetamidoterephthalate | 30 | 70 | 70 | 81:19 | [12] |
| 14 | [Zn ₂ (L1) ₂ (L2)] _n .2n(DMF) L1 = 4-(pyridin-4-ylcarbamoyl)benzoate L2 = benzene dicarboxylate | 48 | 70 | 77 | 78:22 | [13] |
| 15 | [La(L1) ₂] _n .1n(DMF)H 3n(DMF) [Ce(L1) ₂] _n .1n(DMF)H 2n(DMF) [Sm(L1) ₂] _n .1n(HCONH ₂)H 2n(HCONH ₂) L1 = 2-acetamidoterephthalate | 36 36 36 | 70 70 70 | 65 67 71 | | [14] |
| 16 | [La(L2)(HL2)(H ₂ O)(DMF) ₂] _n [Ce(L2)(HL2)(H ₂ O)(DMF) ₂] _n L2 = 2-benzamidoterephthalate | 36 36 | 70 70 | 57 59 | | |
| 17 | [{Cu(L)(DMF)} ₂ .DMF.H ₂ O] _n L = 5-((pyridin-4-ylmethyl)-amino)isophthalate | 40 | 75 | 84 | 78:22 | [15] |

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