Supporting Information

Zinc Metal Organic Frameworks: Efficient Catalysts for Diastereoselective Henry Reaction and Transesterification

Anirban Karmakar, M. Fátima C. Guedes da Silva and Armando J. L. Pombeiro*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisbon, Portugal. E-mail: pombeiro@tecnico.ulisboa.pt

Figure S1: Recycling experiments for 2 (A) of 3 (B) used as catalyst in the Henry reaction (black lines refer to the 1\textsuperscript{st} cycle and red lines to the 2\textsuperscript{nd} cycle).
Figure S2: A) FT-IR spectra of 1 before (black line) and after (red line) the Henry reaction. B) FT-IR spectra of 2 before (black line) and after (red line) the transesterification reaction.
Figure S3: A) PXRD diffractograms of 1 before (red line) and after (blue line) the Henry reaction. B) PXRD diffractograms of 2 before (red line) and after (blue line) the transesterification reaction. The black lines are the calculated ones associated with the respective crystal structures.

Figure S4: A) FT-IR spectra of 2. B) FT-IR spectra of 3. The black and red lines were taken before and after the Henry reaction, respectively.
Figure S5: PXRD diffractograms of 3 [the red line refers to experimental line and the black line is theoretical one].
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### Table S2: Hydrogen bond geometry (Å, °) in compounds 1, 2 and 3.

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### Table S3: Selected bond distances (Å) and angles (°) for compounds 1, 2 and 3

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Symmetry codes to generate equivalent atoms: i) 2-x,1/2+y,3/2-z; ii) 2-x,2-y,1-z; iii) 2-x,-1/2+y,3/2-z

### Table S4: Comparison of bond distances and angles of compound 1-3

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<td>1.929(3) Å - 2.113(2) Å</td>
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<td>Zn-Zn</td>
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<td>98.80(10)° - 127.40(13)°</td>
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<td>Value 3</td>
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<td>&lt;O-Zn-O</td>
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<td>$81.20(10)^\circ - 174.23(10)^\circ$</td>
<td>$95.27(9)^\circ - 120.39(10)^\circ$</td>
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</table>
In compound 1 the bite angles between the planes of the pyridine rings in each bipyridine ligand depends on their coordination modes: while in the monodentate ligand those planes are twisted 24.66°, in the chelating moiety that value is 53.52°. In addition, the mean least-square planes of the two bipyridine ligands are relatively positioned in angles of 78.51°. Concerning the two independent benzodicarboxylate groups, the planes of their phenyl rings make angles of 32.91°. The torsion angles between the phenyl rings and the carboxylate groups are in the 18.0(5) – 6.7(5) ° (absolute value) range. The eight membered Zn$_2$C$_2$O$_4$ core is nearly planar (the maximum deviation from the least-mean square plane for O9 is 0.206 Å) and this plane makes angles of 82.81 and 33.83° with the mean planes of the coordinated bridging and non-bridging bpy ligands, respectively, and 19.82 or 15.00° with the phenyl rings of the dicarboxylate ligands.

![Figure S6: Hydrogen bonded packing diagram of 1](image)
Figure S7. Example of integration in the $^1$H-NMR spectrum for the determination of Henry reaction products (Table 1, entry 8).

**Calculation of the yield and selectivity for compound 1 in the Henry reaction**

Total amount of compounds at the end (see Fig. S5):

Bezaldehyde + *anti* + *syn* = 1 + 5.37 + 14.28 = 20.65

Percentage of the unreacted bezaldehyde: $100/20.65 = 4.8\%$

Conversion of benzaldehyde = yield of $\beta$-nitroalkanols = 100 – 4.8 = 95.2 %.
Yield of *anti*: $100/20.65 \times 5.37 = 26.0\%$

Yield of *syn*: $100/20.65 \times 14.28 = 69.2\%$

**Selectivity:**
Sum of *anti* + *syn* = 26.0 + 69.2 = 95.2.
Selectivity of *anti*: $100/95.2 \times 26 = 27$
Selectivity of *syn*: $100/95.2 \times 69.2 = 73$
**Calculation of the yield for compound 2 in the transesterification reaction**

The methyl peak of methyl-3-nitrobenzoate (reactant) appears as 3.978 ppm and the methyl of ethyl-3-nitrobenzoate (product) appears at 1.425 ppm.

Total amount of compound: unreacted methyl-3-nitrobenzoate + ethyl-3-nitrobenzoate = 1+35.4 = 36.4

Percentage of the unreacted methyl-3-nitrobenzoate: 2.7%

Conversion of methyl-3-nitrobenzoate = yield of ethyl-3-nitrobenzoate = 100-2.7 = 97.2%

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**Figure S8. Example of integration in the $^1$H-NMR spectrum for the determination of transesterification reaction products (Table 4, Entry 7).**

[P= Product peak (from ethyl group of ethyl-3-nitrobenzoate), R= Unreacted methyl-3-nitrobenzoate (methyl group of methyl-3-benzoate), S= Solvent peak]