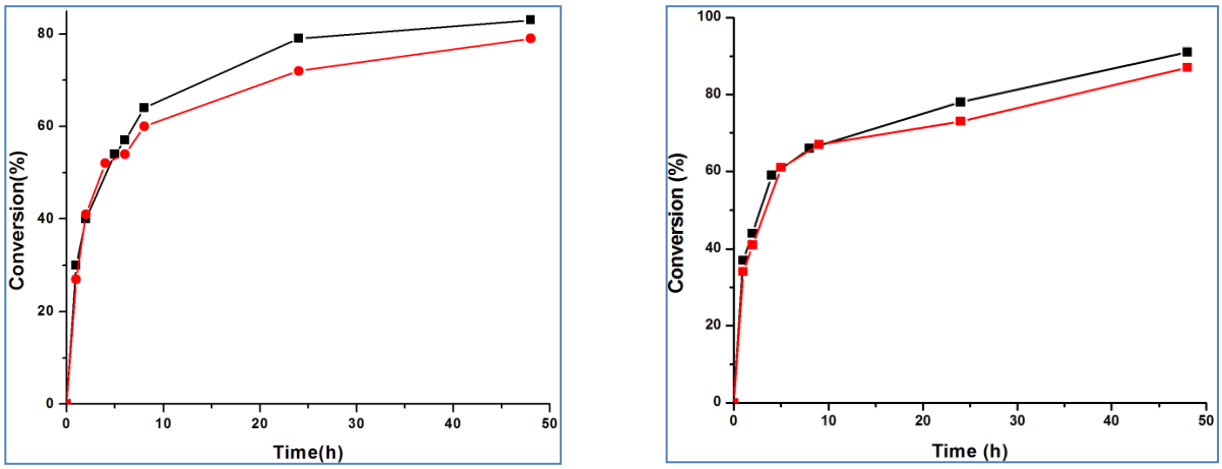
Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

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

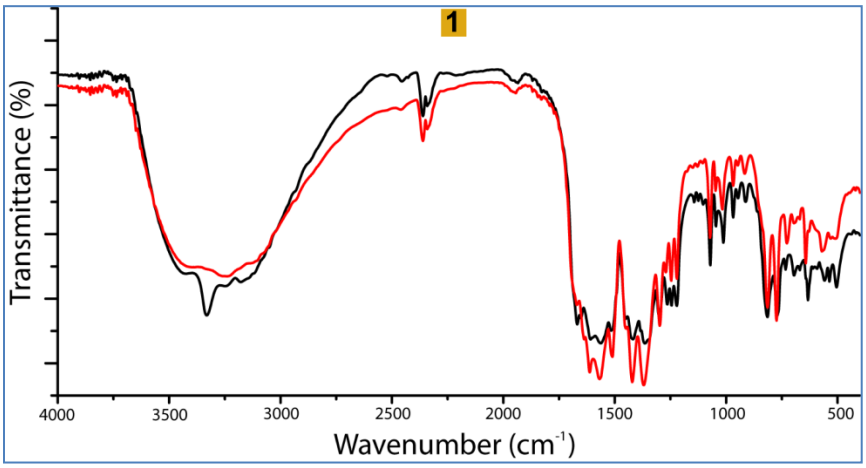
**Anirban Karmakar, M. Fátima C. Guedes da Silva and Armando J. L. Pombeiro***

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*

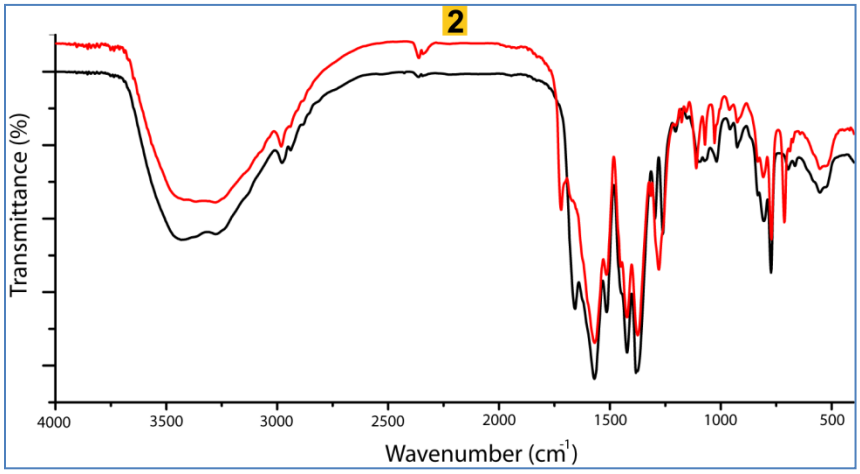



A B

Figure S1: Recycling experiments for **2** (A) of **3** (B) used as catalyst in the Henry reaction (black lines refer to the 1st cycle and red lines to the 2nd cycle).

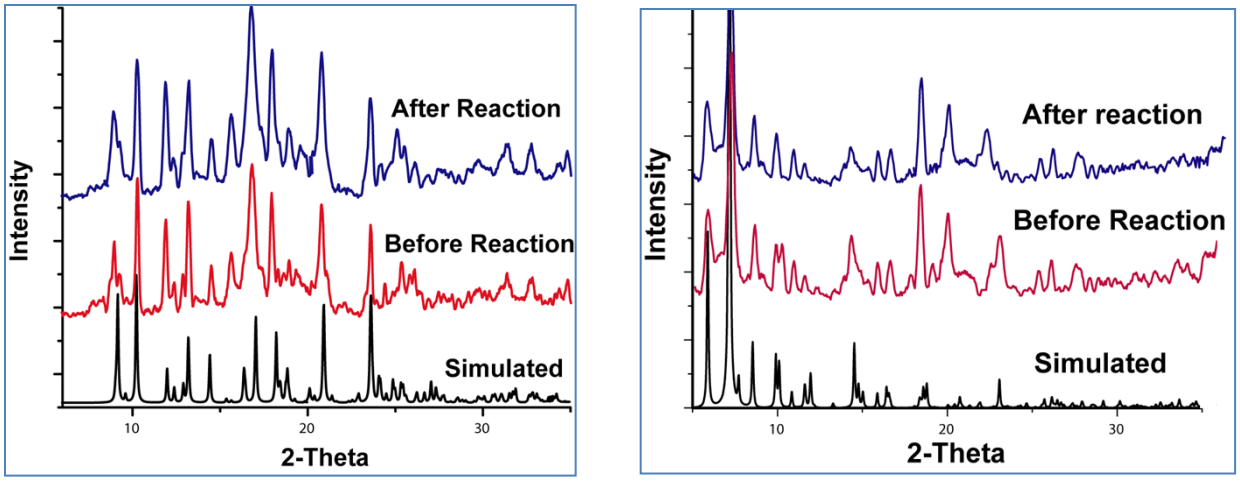



A



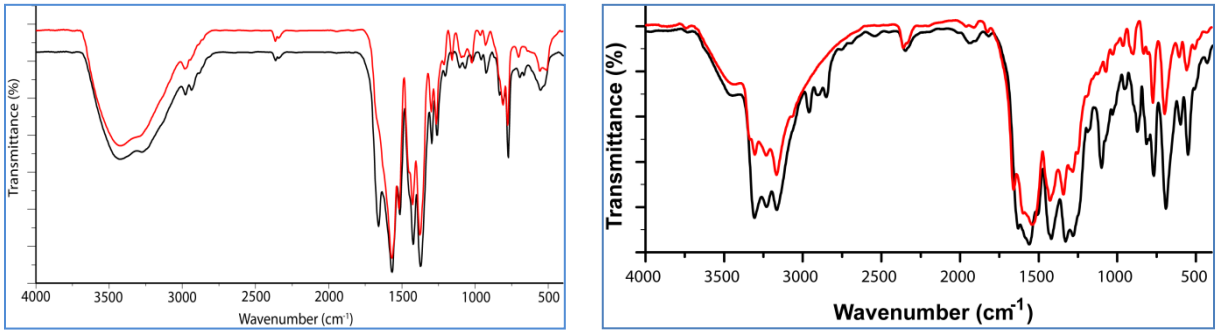

B

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.




**A** **B**

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.




A B

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.

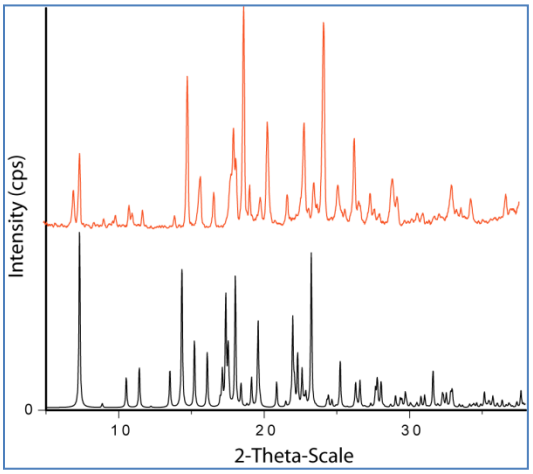


Figure S5: PXRD diffractograms of **3** [the red line refers to experimental line and the black line is theoretical one].

| Table S1: Crystal data and structure refinement details for 1, 2 and 3 | | | |
|---|---|---|---|
| Identification name | **1** | **2** | **3** |
| Formulae | $C_{43}H_{39}N_7O_{12}Zn_2$ | $C_{39}H_{47}N_5O_{21}Zn_4$ | $C_{17}H_{17}NO_8Zn$ |
| Mol. wt. | 976.55 | 1183.30 | 428.68 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| Temperature /K | 296 | 150 | 296 |
| Wavelength /Å | 0.71073 | 0.71073 | 0.71073 |
| *a* /Å | 18.4237(10) | 15.4488(6) | 6.2898(3) |
| *b* /Å | 11.3275(6) | 18.1141(7) | 19.3555(11) |
| *c* /Å | 19.4776(9) | 17.5541(7) | 14.9434(8) |
| β/° | 90.1460(10) | 103.171(3) | 90.931(2) |
| V/ Å$^3$ | 4064.9(4) | 4783.1(3) | 1819.00(17) |
| Z | 4 | 2 | 4 |
| Density/Mgm$^{-3}$ | 1.596 | 0.822 | 1.565 |
| Abs. Coeff. /mm$^{-1}$ | 1.256 | 1.033 | 1.395 |
| F(000) | 2008 | 1208 | 880 |
| Refl. collected | 70544 | 33504 | 20191 |
| Refl. unique | 8345 | 10561 | 3345 |
| Max. 2θ/° | 26.44 | 27.15 | 25.37 |
| Rint | 0.1516 | 0.0595 | 0.0354 |
| Ranges (h, k, l) | -23 <= h <=23<br>-14 <= k <=14<br>-22 <= l <= 24 | -19 <= h <=18<br>-23 <= k <=21<br>-21 <= l <= 22 | -7 <= h <= 7<br>-23 <= k <= 23<br>-17 <= l <= 18 |
| Complete to 2θ (%) | 99.7 | 99.6 | 99.9 |
| Refl. with I > 2σ(I) | 5071 | 5565 | 2705 |
| Data/ Restraints/Parameters | 8345 / 0 / 580 | 10561/ 85 / 358 | 3345/ 4/ 256 |
| Goof ($F^2$) | 0.920 | 0.885 | 1.085 |
| R1 [I > 2s(I)] | 0.0503 | 0.0579 | 0.0401 |
| wR2 [I > 2s(I)] | 0.1042 | 0.1559 | 0.1003 |
| R1 [all data] | 0.1135 | 0.0996 | 0.0525 |
| wR2 [all data] | 0.1042 | 0.1708 | 0.1058 |

| Table S2: Hydrogen bond geometry (Å, °) in compounds 1, 2 and 3. | | | | | | |
|---|---|---|---|---|---|---|
| Compound | D-H---A | D-H (Å) | H···A (Å) | D···A (Å) | <D–H···A(°) | Symmetry |
| **1** | N1-H1····O2 | 0.86 | 1.90 | 2.611(5) | 139 | - |
| | N2-H2····O7 | 0.86 | 1.90 | 2.616(4) | 139 | - |
| | O12-H12A····O4 | 0.910 | 2.070 | 2.971(4) | 171 | x,1.5-y,-1/2+z |
| | O12-H12B····O10 | 1.010 | 1.830 | 2.810(5) | 161 | x,1.5-y,1/2+z |
| | C4-H4····O5 | 0.93 | 2.30 | 2.902(5) | 122 | - |
| | C8-H8····O1 | 0.93 | 2.42 | 2.745(4) | 100 | - |
| | C13-H13····O6 | 0.93 | 2.39 | 2.730(5) | 101 | - |
| | C17-H17····O10 | 0.93 | 2.26 | 2.875(5) | 123 | - |
| | C52-H52B····O11 | 0.961 | 2.40 | 2.792(8) | 104 | - |
| | | | | | | |
| **2** | N1-H1····O2 | 0.88 | 1.96 | 2.667(6) | 136 | - |
| | N21-H21····O22 | 0.88 | 1.89 | 2.595(8) | 136 | - |
| | O31-H31O····O21 | 0.810 | 1.94 | 2.744(4) | 172 | -x,-y,1-z |
| | C3-H3····O1 | 0.951 | 2.40 | 2.726(6) | 100 | - |
| | C6-H6····O3 | 0.949 | 2.22 | 2.874(7) | 125 | - |
| | C24-H24····O21 | 0.950 | 2.45 | 2.77(2) | 100 | 1-x,-y,1-z |
| | C24-H24····O23 | 0.950 | 2.35 | 3.00(2) | 125 | - |
| | | | | | | |
| **3** | N1-H1····O1 | 0.86 | 1.91 | 2.619(3) | 139 | |
| | O10-H10C····O30 | 0.908 | 2.26 | 3.155(3) | 167 | -1+x,y,z |
| | O20-H20C····O4 | 0.923 | 2.18 | 3.047(3) | 156 | x,1/2-y,-1/2+z |
| | O10-H10D····O2 | 0.933 | 2.09 | 3.005(3) | 168 | -1+x,y,z |
| | O20-H20D····O4 | 0.884 | 2.18 | 3.018(3) | 158 | 1-x,1/2+y,1/2-z |
| | C3-H3····O2 | 0.930 | 2.44 | 2.770(4) | 101 | - |
| | C6-H6····O4 | 0.931 | 2.50 | 2.806(3) | 100 | - |
| | C6-H6····O5 | 0.931 | 2.23 | 2.861(4) | 124 | - |
| | C17-H17····O5 | 0.929 | 2.45 | 2.767(4) | 100 | - |

| Table S3: Selected bond distances (Å) and angles (°) for compounds 1, 2 and 3 | | | | | |
|---|---|---|---|---|---|
| **1** | | | | | |
| | Bond distances | | Bond angles | | Bond angles |
| Zn1-N5 | 2.154(3) | <O8-Zn1-O9 | 107.05(10) | <N6 -Zn1-O3 | 89.41(10) |
| Zn1-N6 | 2.154(3) | <O8-Zn1-N6 | 97.01(11) | <N5-Zn1-O4 | 87.77(11) |
| Zn1-O3 | 2.294(3) | <O8-Zn1-N5 | 93.37(11) | <N5-Zn1-O3 | 83.40(10) |
| Zn1-O4 | 2.163(3) | <O8-Zn1-O4 | 90.77(10) | <O4-Zn1-O3 | 59.19(10) |
| Zn1-O8 | 2.019(2) | <O8-Zn1-O3 | 149.83(11) | <O6-Zn2-O1 | 103.53(12) |
| Zn1-O9 | 2.041(3) | <O9-Zn1-N6 | 88.82(11) | <O6-Zn2-O12 | 91.35(12) |
| Zn2-O11 | 2.347(3) | <O9-Zn1-N5 | 84.63(11) | <O6-Zn2-O11 | 86.00(12) |
| Zn2-O12 | 2.141(3) | <O9-Zn1-O4 | 160.96(10) | <O6-Zn2-N3 | 127.76(13) |
| Zn2-N3 | 2.048(4) | <O9-Zn1-O3 | 102.51(11) | <O1-Zn2-N3 | 128.06(13) |
| Zn2-O1 | 1.980(3) | <N6-Zn1-N5 | 168.99(11) | <O1-Zn2-O11 | 88.00(13) |
| Zn2-O6 | 1.960(3) | <N6-Zn1-O4 | 95.72(11) | <O1-Zn2-O12 | 93.95(13) |
| | | <N3-Zn-O12 | 92.59(14) | <N3-Zn2-O11 | 87.97(13) |
| | | <O12-Zn2-O11 | 177.03(12) | | |
| **2** | | | | | |
| Zn1-O1 | 2.101(3) | <O51$^{ii}$-Zn1-O11$^{i}$ | 174.23(10) | <O41-Zn1-O1 | 83.70(12) |
| Zn1-O11$^{i}$ | 2.077(3) | <O51-Zn1-O41$^{ii}$ | 93.49(12) | <O41-Zn1-O51 | 173.99(12) |
| Zn1-O31 | 2.096(3) | <O51-Zn1-O31$^{ii}$ | 91.02(12) | <O51-Zn2-O22 | 117.85(12) |
| Zn1-O41 | 2.093(3) | <O51-Zn1-O1$^{ii}$ | 88.22(11) | <O51-Zn2-O2 | 113.16(11) |
| Zn1-O51$^{ii}$ | 2.070(3) | <O51-Zn1-O51$^{ii}$ | 81.20(10) | <O51-Zn2-O12$^{i}$ | 106.21(11) |
| Zn1-O51 | 2.113(2) | <O11$^{i}$-Zn1-O51 | 93.28(10) | <O31-Zn1-O51 | 93.85(10) |
| Zn2-O2 | 1.946(3) | <O11-Zn1-O1$^{i}$ | 93.78(12) | <O31-Zn1-O1 | 172.62(10) |
| Zn2-O12$^{iii}$ | 1.967(3) | <O11-Zn1-O41$^{i}$ | 92.11(12) | <O22-Zn2-O2 | 106.76(12) |
| Zn2-O22 | 1.937(2) | <O11-Zn1-O31$^{i}$ | 87.69(12) | <O22-Zn2-O12$^{i}$ | 103.92(12) |
| Zn2-O51 | 1.929(3) | <O41-Zn1-O31 | 89.03(12) | <O1-Zn1-O51 | 93.28(10) |
| | | <O2-Zn2-O12$^{i}$ | 108.21(12) | <Zn2-O51-Zn1$^{ii}$ | 127.40(13) |
| | | <Zn2-O51-Zn1 | 101.19(12) | <Zn1-O51-Zn1$^{ii}$ | 98.80(10) |
| 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 | | | | | |
| **3** | | | | | |
| Zn1-O1 | 1.9766(18) | <O3-Zn1-O1 | 95.27(9) | <O1-Zn1-O10 | 104.34(10) |
| Zn1-O3 | 1.9713(18) | <O3-Zn1-O20 | 103.54(10) | <O20-Zn1-O10 | 114.81(11) |
| Zn1-O10 | 2.015(2) | <O1-Zn1-O20 | 120.39(10) | | |
| Zn1-O20 | 2.009(2) | <O3-Zn1-O10 | 117.59(9) | | |
| | | | | | |

| Table S4: Comparison of bond distances and angles of compound 1-3 | | | |
|---|---|---|---|
| | **1** | **2** | **3** |
| Zn-O | 1.960(3)Å - 2.347(3)Å | 1.929(3)Å - 2.113(2)Å | 1.9713(18)Å - 2.015(2) Å |
| Zn-N | 2.048(4)Å - 2.154(3)Å | - | - |
| Zn-Zn | 4.5137(6)Å - 9.9093(7)Å | 3.1250(7)Å - 3.1759(6)Å | 11.1409(6)Å |
| <Zn-O-Zn | - | 98.80(10)°- 127.40(13)° | - |

| | | | |
|---|---|---|---|
| <N-Zn-N | 92.59(14)° - 168.99(11)° | - | - |
| <O-Zn-O | 59.19(10)° - 177.03(12)° | 81.20(10)° - 174.23(10)° | 95.27(9)°- 120.39(10)° |

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 $Zn_2C_2O_4$ 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.

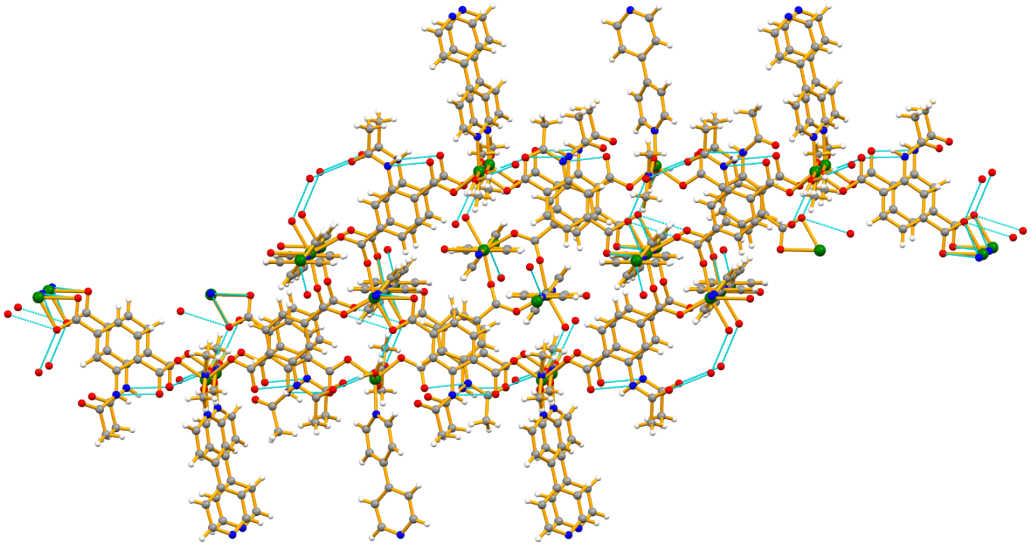


Figure S6: Hydrogen bonded packing diagram of **1**

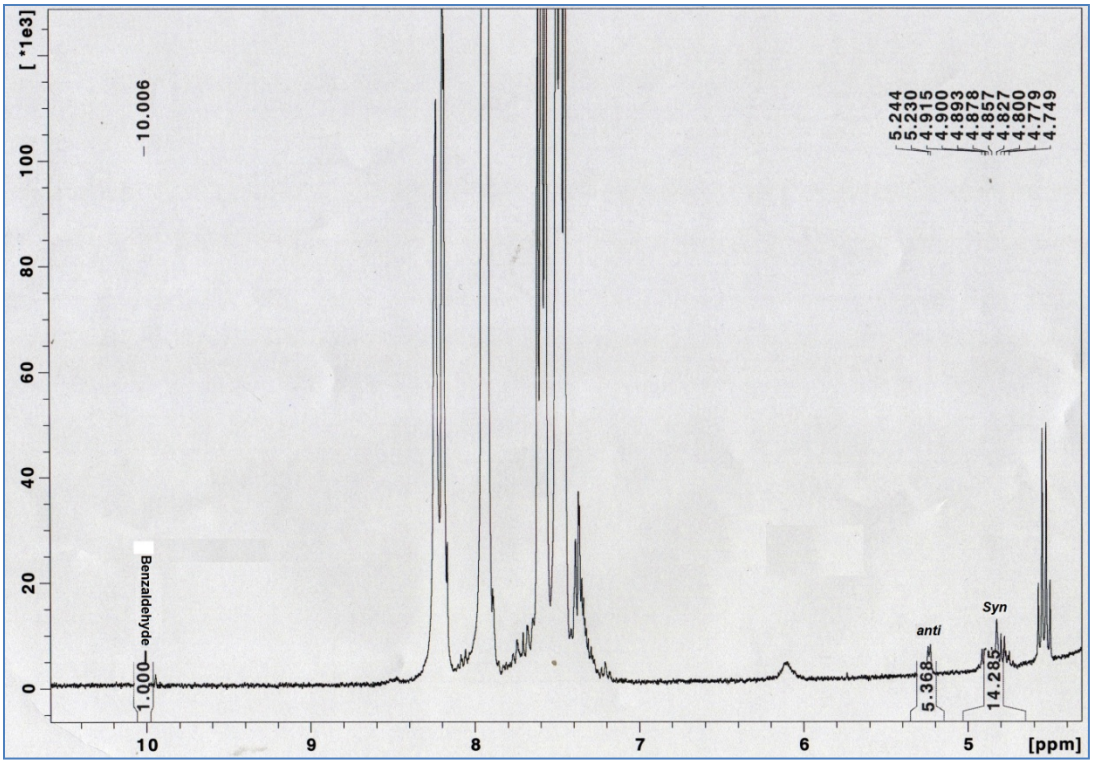



Figure S7**.** Example of integration in the $^{1}$H-NMR spectrum for the determination of Henry reaction products (Table 1, entry 8).

## *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 β-nitroalkanols = 100 – 4.8 = 95.2 %.
Yield of *anti*: 100/20.65x5.37 = 26.0%

Yield of *syn*: 100/20.65x14.28 = 69.2%

***Selectivity*:**
Sum of *anti* + *syn* = 26.0+ 69.2 = 95.2.
Selectivity of *anti*: 100/95.2x26= 27
Selectivity of *syn*: 100/95.2x69.2= 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%

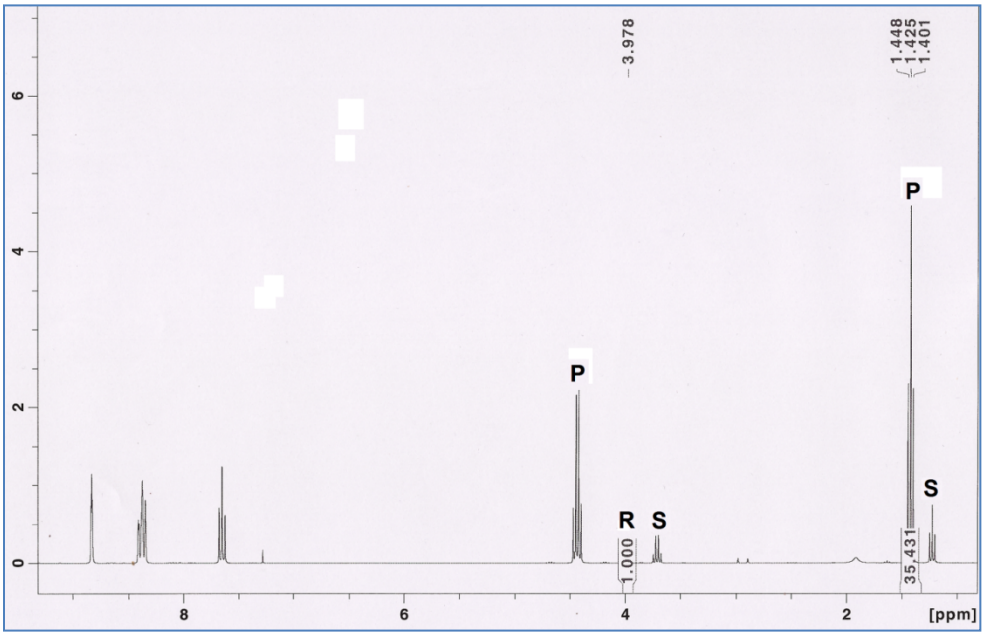



Figure S8. Example of integration in the $^{1}$H-NMR spectrum for the determination of transesterification reaction products (Table 4, Entry 7). [P= Product peak (from ethyl group of ethyl-3-nitrobenzoate), R= Unreacted methyl-3-nitrobenzoate (methyl group of methyl-3-benzoate), S= Solvent peak]