Electronic Supplementary Material:

Montmorillonite K10-catalyzed solvent-free conversion of furfural into cyclopentenones

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Experimental section

All chemicals and solvents were purchased from common commercial sources and were used as received without any further purification. Montmorillonite K10 clay was obtained from Sigma-Aldrich, and it has the following chemical composition (wt %) SiO_2: 67.6; Al_2O_3: 14.6; Fe_2O_3: 2.9; MgO: 1.8.

All reactions were monitored by GC-MS. The GC-MS Shimadzu workstation constituted of a GC 2010 (equipped with a 30 m-QUADREX 007-5MS capillary column, operating in "split" mode, with 1 $mL \cdot min^{-1}$ flow of He as carrier gas).

Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Brüker spectrometer at 300 MHz. Chemical shifts are reported in δ units (ppm) with tretramethylsilane (TMS) as the reference (δ 0.00). All coupling constants (*J*) are reported in hertz. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Brüker at 75 MHz. Chemical shifts are reported in δ units (ppm) relative to $CDCl_3$ (δ 77.0).

MW-assisted reactions were performed on a Synthos 3000 instrument from Anton Paar, equipped with a 4 × 24MG5 Rotor, with an IR probe for external temperature control.

General Experimental Procedure for the Microwave-Assisted Cyclization Rearrangement of Furfural and Amines.

Morpholine (2 mmol) was added to a stirred solution of furfural (1 mmol) and MK10 (20 mg). The resulting mixture was reacted for 5 min in a Synthos 3000 microwave instrument, at a temperature value of 60 °C (IR limit).

After completion of the reaction (monitored by GCMS), the MK10 was separated from the reaction mixture by filtration, and washed with ethyl acetate (3 mL) four times. The products were isolated after the evaporation of the solvent, to yield compounds at 90–99 % yields. Spectral data were in accordance with the literature [61].

The reaction of morpholine with furfural was scaled up to grams, using 20 mmol of furfural and 40 mmol of morpholine, with amount corresponding to MK10. After the

completion of the reaction and the separation of MK10, the products were obtained at a yield of 97%.

***trans*-4,5-dimorpholinecyclopent-2-en-1-one:** Spectral data were in accordance with the literature [61].

***trans*-4,5-di(pyrrolidin-1-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [61] .

***trans*-4,5-di(piperidin-1-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [61].

***trans*-4,5-di(isoindolin-2-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature[61].

***trans*-4,5-bis(diisobutylamino)cyclopent-2-enone:** Spectral data were in accordance with the literature [56].

***trans*-4,5-bis(diallylamino)cyclopent-2-enone:** Spectral data were in accordance with the literature [56].

***trans*-4,5-bis(dibenzylamino)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [61].

***trans*-4,5-bis(allyl(phenyl)amino)cyclopent-2-enone**: Spectral data were in accordance with the literature [56].

***trans*-4,5-bis(methyl(phenyl)amino)cyclopent-2-enone**: Spectral data were in accordance with the literature [56].

General protocol for the synthesis of 2,4 dimorpholinecyclopent-2-enones.

After perfoming the reported procedure for 4,5-trans-dimorpholinecyclopen-2-enone, we added 0.2 mmol of morpholine to the reaction mixture and kept it at room temperature for another hour. After completion, ethyl acetate was added (3 mL), the catalyst was filtered, and

the product isolated after evaporation of the solvent, to yield 2,4-dimorpholinecyclopent-2-enone at an efficiency of 99%. Spectral data were in accordance with the literature [61].