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

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**Electronic Supplementary Material**

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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 obtained from Aldrich, has the following chemical composition (wt%) SiO2: 67.6; Al2O3: 14.6; Fe2O3: 2.9; MgO: 1.8.

All reactions were monitored by GC-MS. The GC-MS Shimadzu workstation was constituted by a GC 2010 (equipped with a 30 m-QUADREX 007-5MS capillary column, operating in the “split” mode, 1 mL min-1 flow of He as carrier gas).

Proton nuclear magnetic resonance (1H-NMR) spectra were recorded on a Brüker spectrometer at 300 MHz. Chemical shifts are reported in δ units (ppm) with tretramethylsilane (TMS) as 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 (13C-NMR) spectra were recorded on a Brüker at 75 MHz. Chemical shifts are reported in δ units (ppm) relative to CDCl3 (δ 77.0).

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

**General Experimental Procedure for Microwave-Assisted Cyclitation rearrangement of furfural and amines.**

The 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, fixed on the 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) for four times. The products were isolated after evaporation of the solvent to afford compounds in 90-99 % yields. Spectral data were in accordance with the literature [57].

The reaction of morpholine with furfural was scaled up to grams using 20 mmol of furfural and 40 mmol of morpholine with amount corresponding of MK10. After completion of the reaction and separation of MK10, the product were obtained with a yield of 97%.

***trans*-4,5-dimorpholinecyclopent-2-en-1-one:** Spectral data were in accordance with the literature [57].

***trans*-4,5-di(pyrrolidin-1-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [57] .

***trans*-4,5-di(piperidin-1-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [57].

***trans*-4,5-di(isoindolin-2-yl)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature[57].

***trans*-4,5-bis(diisobutylamino)cyclopent-2-enone:** Spectral data were in accordance with the literature [55].

***trans-*4,5-bis(diallylamino)cyclopent-2-enone:** Spectral data were in accordance with the literature [52].

***trans*-4,5-bis(dibenzylamino)cyclopent-2-en-1-one:** Spectral data were in accordance with the literature [57].

***trans*-4,5-bis(allyl(phenyl)amino)cyclopent-2-enone**: Spectral data were in accordance with the literature [52].

***trans*-4,5-bis(methyl(phenyl)amino)cyclopent-2-enone**: Spectral data were in accordance with the literature [52].

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

After perfomed the 4,5-trans-dimorpholinecyclopen-2-enone as the reported procedure, to reaction mixture we added 0,2 mmol of morpholine and kept at room temperature for further 1 hour. After completion, ethyl acetate was added (3 mL), the catalyst was filtrate and the product isolate after evaporation of the solvent to afford 2,4-dimorpholinecyclopent-2-enone in 99 % yields. Spectral data were in accordance with the literature [57].