

## Supplementary data

### Highly regioselective terminal alkynes hydroformylation and Pauson-Khand reaction catalysed by mesoporous organised Zirconium oxide based powders.

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#### 1- Hydroformylation conditions

All hydroformylation reactions were carried out in a magnetically stirred 100 ml stainless steel autoclave, fitted, when compatible with the reaction conditions, with a clean glass vessel.

For 2,3-dimethylbutene: In a typical run, an autoclave containing a suspension of 700 mg of 2,3-dimethylbut-1-ene (8.4 mmol) and 50 mg of ZS20c (0.4 mmol) in 20 ml of toluene, was pressurized with 30 bars of syngas, heated to 110°C and allowed to react for 48 h.

For 2-octene : In a typical run, an autoclave containing a suspension of 900 mg of 2-octene (8 mmol) and 50 mg of ZS20c (0.4 mmol) in 20 ml of toluene, was pressurized with 30 bars of syngas, heated to 110°C and allowed to react for 48 h.

For styrene: As the reaction conditions are relatively mild, the autoclave could be fitted with clean glass vessel. In a typical run, an autoclave containing a suspension 425 mg of styrene (4 mmol) and 50 mg of ZS20c (0.4 mmol) in 20 ml of toluene, was pressurized with 20 bars of syngas, heated to 60°C and allowed to react for 24 h.

For the alkynes hydroformylations the reactions conditions are specified in the paper. In typical runs, 50 mg of ZS20c were suspended in 20 ml toluene solutions of the corresponding amount of the desired alkyne and placed in the autoclave. In those cases the use of glass vessel was not possible.

#### 2- Pauson-Khand reaction conditions.

The conditions are specified in the paper. In typical runs, 50 mg of ZS20c (0.4 mmol) were suspended in 20 ml toluene solutions of the corresponding amount of the desired alkyne and 820 mg (10 mmol) of cyclohexen and placed in the autoclave. In those cases the use of glass vessel was not possible.