

Cite this: DOI: 10.1039/c0xx00000x  
www.rsc.org/xxxxxx

### Supplementary Informations

#### **Silver-zeolite catalysed solvent-free synthesis of (spiro)ketals**

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## 1. General Information

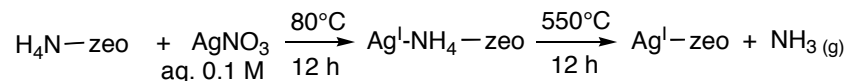
Reagents and solvents were purified using standard means. All other chemicals were used as received except where otherwise noted in the experimental text. All other extractive procedures were performed using non-distilled solvents and all aqueous solutions used were saturated (satd).

Analytical Thin Layer Chromatography (TLC) were carried out on silica gel 60 F<sub>254</sub> plates with visualization by ultra violet, KMnO<sub>4</sub>, *p*-anisaldehyde or molybdophosphoric acid/Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O. Flash column chromatographies were carried out using silica gel 60 (40-63 μm) and mixtures of diethyl ether and *n*-pentane as eluents. Evaporations of solvents were conducted under reduced pressure *in vacuo*. at temperatures less than 30 °C.

Proton (<sup>1</sup>H NMR) and Carbon (<sup>13</sup>C NMR) nuclear magnetic resonance spectra were recorded on Bruker Avance Spectrometers at 75, 300, 400 or 500 MHz. Chemical shifts are given in part per million (ppm) on the delta scale. The solvent peak was used as reference value. For <sup>1</sup>H NMR : CDCl<sub>3</sub> = 7.26 ppm or C<sub>6</sub>D<sub>6</sub> = 7.16 ppm. For <sup>13</sup>C NMR : CDCl<sub>3</sub> = 77.0 ppm or C<sub>6</sub>D<sub>6</sub> = 128.0 ppm. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sext = sextuplet, m = multiplet), coupling constants (J/Hz) and integration. X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Advance diffractometer, with a Ni detector side filtered Cu K $\alpha$  radiation (1.5406 Å) over a 2 $\theta$  range of 5-60 ° and a position sensitive detector using a step size of 0.02 ° and a step time of 2 s. Infrared spectra were recorded neat on an ALPHA Bruker FT-IR apparatus. Wavelengths of maximum absorbance ( $\nu_{\max}$ ) are quoted in wave numbers (cm<sup>-1</sup>). XPS spectra were obtained using a Multilab 2000 XPS (Thermo). The pressure inside the chamber was 5.10<sup>-9</sup> mbar during the analysis and the incident beam was AlK $\alpha$  radiation (h $\nu$  1486.6 eV). The spectra were calibrated relative to the C 1s<sub>1/2</sub> binding energy of carbon contamination at 284.6 eV. SEM images were acquired with a Hitachi S4800 FEG microscope equipped with an EDS system (EDX) for elemental analysis. EDX spectra were acquired using 20 kV primary electron voltage to determine the composition of the material. Mass spectra were recorded by ElectroSpray Ionization (ESI) or Electronic Impact (EI).

## 2. Ag-zeolite Preparation

Preparation procedure and characterization of Ag-zeolites are only provided here for the more effective catalyst Ag<sup>I</sup>-USY.<sup>1</sup> The other Ag-zeolites screened in this work (see Fig 1) were prepared using the same standard methods from commercial zeolites (mordenite, ZSM-5, beta).



**Equation 1.** Preparation of Ag-doped zeolites by ion-exchange

Ag<sup>I</sup>-USY was prepared using standard ion-exchange method<sup>2</sup>. Commercial NH<sub>4</sub>-USY (CBV500 Zeolyst international, Si/Al = 2.8, 2.0 g) was exchanged by mixing the material with a 0.1 M aqueous AgNO<sub>3</sub> solution (50 mL). The resulting white suspension was vigorously stirred overnight at 80 °C in the dark. After the first ion-exchange, the solution was cooled, filtered through nylon membrane (0.2 μm), washed with copious amounts of water and dried in an oven for 24 h at 110 °C. The resulting white solid was then submitted to a second ion-exchange by following the same procedure described above. After drying for 24 h at 110 °C, the resulting white powder was finally calcinated at 550 °C overnight.

### 3. Ag-zeolites Characterization

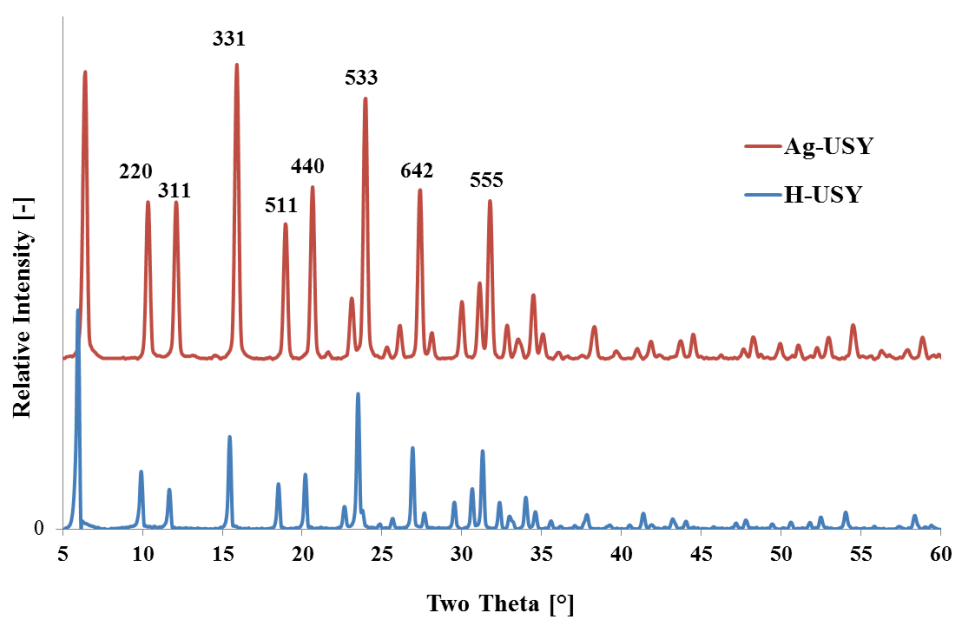
#### Elemental analysis (ICP)

**Table 1.** Elemental analysis of Ag-USY and Ag-ZSM5

| Ag-zeolite | preparation | Si [w%] | Al [w%] | Ag [w%] | Si/Al <sup>a</sup> | Ag [mmol/g] <sup>b</sup> |
|------------|-------------|---------|---------|---------|--------------------|--------------------------|
| Ag-USY     | 1 ion-exch. | 29.56   | 9.65    | 9.33    | 3.06               | 0.86                     |
| Ag-USY     | 2 ion-exch. | 28.75   | 9.49    | 10.96   | 3.03               | 1.02                     |
| Ag-ZSM5    | 2 ion-exch. | 38.89   | 2.31    | 5.25    | 16.84              | 0.49                     |

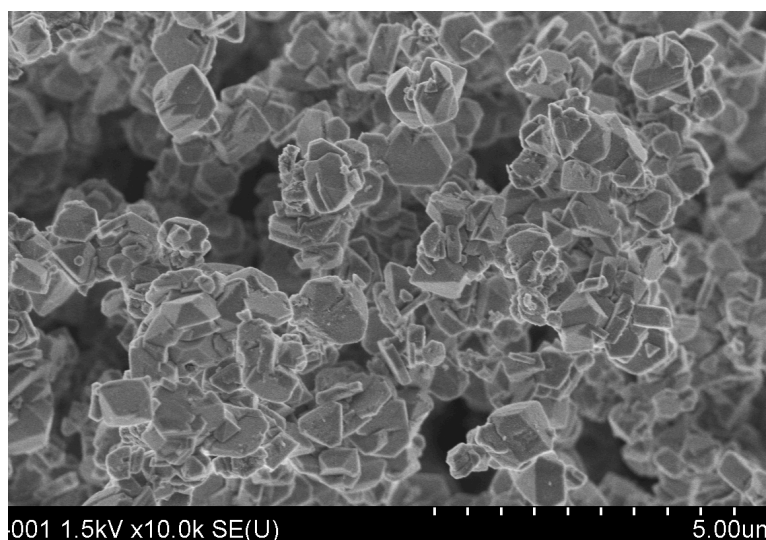
<sup>a</sup> Calculated from Si and Al w% values. <sup>b</sup> Calculated from Ag w% values.

#### Powder-XRD



**Figure 1.** XRD patterns of H-USY and Ag-USY (two ion-exchanges)

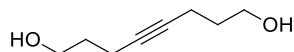
#### SEM-EDX



**Figure 2.** SEM micrograph of Ag-USY (two ion-exchanges)

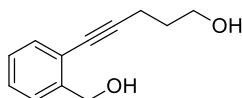
#### 4. Synthesis of Alkynediols 1d-h.

Alkynediols **1d-h** were synthesized according to procedures reported elsewhere and were already fully characterized.



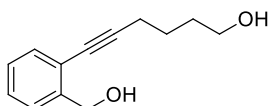
##### **Oct-4-yne-1,8-diol 1d.**<sup>3</sup>

Yield: 26% in 3 steps; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ =3.76-3.70 (m, 4 H), 2.26 (t,  $J$ =6.9, 4 H), 1.76-1.67 (m, 4 H), 1.57 ppm (br s, 2 H, 2 OH).



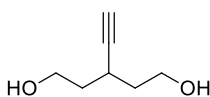
##### **5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-ol 1e.**<sup>4</sup>

Yield: 90%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ =7.37-7.34 (m, 2 H), 7.24-7.17 (m, 2 H), 4.78 (s, 2 H), 3.73 (t,  $J$ =6.4, 2 H), 3.18 (br s, 2 H, 2 OH), 2.51 (t,  $J$ =6.8, 2 H), 1.91-1.82 ppm (m, 2 H).



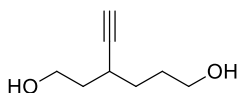
##### **6-(2-(hydroxymethyl)phenyl)hex-5-yn-1-ol 1f.**<sup>5</sup>

Yield: 61%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ =7.40-7.17 (m, 4 H), 4.76 (s, 2 H), 3.71-3.66 (m, 2 H), 2.48 (t,  $J$ =6.5, 2 H), 1.93 (br s, 2 H, 2 OH), 1.76-1.67 ppm (m, 4 H).



##### **3-ethynylpentane-1,5-diol 1g.**<sup>4</sup>

Yield: 18% in 2 steps; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ =3.82 (t,  $J$ =6.4, 4 H), 2.82-2.72 (m, 1 H), 2.12 (d,  $J$ =2.6, 1 H), 1.83-1.64 ppm (m, 4 H).



##### **3-ethynylhexane-1,6-diol 1h.**<sup>4</sup>

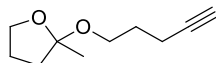
Yield: 13% in 2 steps; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$ =3.83 (t,  $J$ =6.0, 2 H), 3.69 (t,  $J$ =6.2, 2 H), 2.59 (m, 1 H), 2.11 (d,  $J$ =2.4, 1 H), 1.89-1.50 ppm (m, 6 H).

#### 5. General Procedure for the Silver-Zeolite Catalysed Synthesis of Ketals

To an alkyne(di)ol or acid (1 mmol) neat or in MeOH (2 mL) was added Ag-USY (0.02 mmol; 2 mol%) at room temperature. The resulting suspension was either maintained at room temperature or warmed in a sealed tube. After reaction completion (monitored by thin-layer chromatography), the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a Nylon membrane (0.2  $\mu$ m). The solvent was removed in vacuum, and the crude residue was purified by flash chromatography (*n*-pentane/Et<sub>2</sub>O).

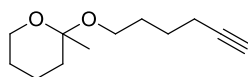
## 6. Characterization of Ketals 3a-h

Ketals **3d-h** are already fully described in the literature.



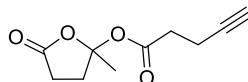
### 2-methyl-2-(pent-4-yn-1-yloxy)tetrahydrofuran **3a**.

Prepared from the *general procedure* in 85% (170 mg, 1.01 mmol) as a colorless oil from pent-4-yn-1-ol (200 mg, 2.38 mmol).  $R_f = 0.81$  (cyclohexane/EtOAc 40 %). IR (neat)  $\nu_{\max}$  3294, 2986, 2941, 2878, 1443, 1377, 1322, 1241, 1199, 1159, 1118, 1092, 1064, 1019, 904, 851, 628  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=3.73\text{-}3.68$  (m, 2 H), 3.58-3.51 (m, 1 H), 3.40-3.33 (m, 1 H), 2.13 (td,  $J=7.0, 2.6$ , 2 H), 1.94-1.74 (m, 2 H), 1.81 (t,  $J=2.7$ , 1 H), 1.67-1.58 (m, 2 H), 1.55-1.41 (m, 2 H), 1.34 ppm (s, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=107.7, 84.5, 69.3, 67.8, 59.4, 38.9, 30.0, 25.2, 22.4, 16.0$  ppm. HRMS (ESI, positive mode):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{16}\text{NaO}_2$  191.105, found 191.104.



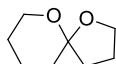
### 2-(hex-5-yn-1-yloxy)-2-methyltetrahydro-2H-pyran **3b**.

Prepared from the *general procedure* in 68% (136 mg, 0.69 mmol) as a colorless oil from hex-5-yn-1-ol (200 mg, 2.04 mmol).  $R_f = 0.67$  (cyclohexane/EtOAc 20 %). IR (neat)  $\nu_{\max}$  3307, 2940, 2870, 1451, 1374, 1269, 1227, 1176, 1088, 1062, 1034, 967, 865, 810, 626  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=3.60\text{-}3.46$  (m, 2 H), 3.42-3.35 (m, 1 H), 3.31-3.24 (m, 1 H), 2.01 (td,  $J=7.1, 2.8$ , 2 H), 1.94-1.76 (m, 1 H), 1.81 (t,  $J=2.7$ , 1 H), 1.72-1.67 (m, 1 H), 1.63-1.45 (m, 4 H), 1.44-1.17 (m, 4 H), 1.23 ppm (s, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=97.6, 84.7, 63.4, 61.6, 59.7, 36.7, 29.9, 26.4, 25.9, 25.3, 19.7, 19.0$  ppm. HRMS (ESI, positive mode):  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{20}\text{NaO}_2$  219.136, found 219.136.



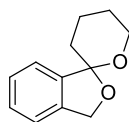
### 2-methyl-5-oxotetrahydrofuran-2-yl pent-4-ynoate **3c**.

Prepared from the *general procedure* in 23% (69 mg, 0.35 mmol) as a colorless oil from pent-4-ynoic acid (300 mg, 3.06 mmol).  $R_f = 0.76$  (EtOAc/cyclohexane 30 %). IR (neat)  $\nu_{\max}$  3286, 2922, 2850, 1787, 1739, 1416, 1385, 1266, 1161, 1117, 1078, 992, 936, 900, 797, 652, 522, 489, 402  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=2.58\text{-}2.46$  (m, 1 H), 2.20-1.94 (m, 6 H), 1.75 (t,  $J=2.4$ , 1 H), 1.56-1.48 (m, 1 H), 1.40 ppm (s, 3 H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta=175.1, 170.2, 109.0, 82.7, 70.0, 34.1, 33.0, 28.9, 26.2, 14.6$  ppm. HRMS (ESI, positive mode):  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{12}\text{NaO}_4$  219.061, found 219.063.



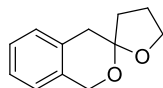
### 1,6-dioxaspiro[4.5]decane **3d**.<sup>6</sup>

Prepared following the *general procedure* in 83% yield.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 300 MHz):  $\delta=3.97\text{-}3.82$  (m, 2 H), 3.78-3.71 (m, 1 H), 3.61-3.54 (m, 1 H), 2.04-1.80 (m, 3 H), 1.66-1.61 (m, 2 H), 1.56-1.38 (m, 4 H), 1.28-1.20 ppm (m, 1 H).



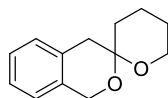
**3',4',5',6'-tetrahydro-3H-spiro[isobenzofuran-1,2'-pyran] 3e.**<sup>4</sup>

Prepared following the *general procedure* in 9% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ=7.32-6.97 (m, 4 H), 5.15 (d, *J*=12.6, 1 H), 4.98 (d, *J*=12.8, 1 H), 4.10-4.04 (m, 1 H), 3.81-3.74 (m, 1 H), 2.22-1.78 ppm (m, 6 H).



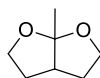
**4,5-dihydro-3H-spiro[furan-2,3'-isochroman] 3e'.**<sup>4</sup>

Prepared following the *general procedure* in 76% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ=7.32-6.97 (m, 4 H), 4.90 (d, *J*=14.9, 1 H), 4.66 (d, *J*=14.9, 1 H), 3.98 (t, *J*=6.6, 2 H), 3.21 (d, *J*=16.3, 1 H), 2.80 (d, *J*=16.4, 1 H), 2.22-1.78 ppm (m, 4 H).



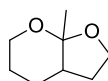
**3',4',5',6'-tetrahydrospiro[isochroman-3,2'-pyran] 3f.**<sup>7</sup>

Prepared following the *general procedure* in 88% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ=7.16-7.10 (m, 2 H), 7.07-6.96 (m, 2 H), 4.79 (d, *J*=14.8, 1 H), 4.67 (d, *J*=14.8, 1 H), 3.76 (td, *J*=11.0, *J*=3.5, 1 H), 3.68-3.62 (m, 1 H), 2.87 (d, *J*=16.5, 1 H), 2.73 (d, *J*=16.5, 1 H), 2.01-1.56 ppm (m, 6 H).



**6a-methylhexahydrofuro[2,3-*b*]furan 3g.**<sup>4</sup>

Prepared following the *general procedure* in 81% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ=3.92 (td, *J*=8.8, *J*=6.2, 2 H), 3.86 (td, *J*=8.8, *J*=3.8, 2 H), 2.49 (tt, *J*=8.8, *J*=3.4, 1 H), 2.21-2.11 (m, 2 H), 1.75-1.67 (m, 2 H), 1.48 ppm (s, 3 H).



**7a-methylhexahydro-2H-furo[2,3-*b*]pyran 3h.**<sup>4</sup>

Prepared following the *general procedure* in 73% yield. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz): δ=4.04-3.96 (m, 1 H), 3.74-3.67 (m, 2 H), 3.37-3.30 (m, 1 H), 1.67-1.50 (m, 3 H), 1.43-1.29 (m, 4 H), 1.39 ppm (s, 3 H).

<sup>1</sup> Full details will be reported in a more specialised journal.

<sup>2</sup> N. D. Hutson, B. A. Reisner, R. T. Yang, B. H. Toby, *Chem. Mater.* **2000**, *12*, 3020-3031.

<sup>3</sup> T. von Hirschheydt, V. Wolfart, R. Gleiter, H. Irgartinger, T. Oeser, F. Rominger, F. Eisenrager, *J. Chem. Soc., Perkin Trans. 2* **2000**, 175-183.

<sup>4</sup> Messerle, B. A.; Vuong, K. Q. *Organometallics* **2007**, *26*, 3031-3040.

<sup>5</sup> K. Ravindar, M. S. Reddy, P. Deslongchamps, *Org. Lett.* **2011**, *13*, 3178-3181.

<sup>6</sup> Ley, S. V.; Lygo, B.; Sternfeld, F.; Wonnacott, A. *Tetrahedron* **1986**, *42*, 4333-4342.

<sup>7</sup> Ho, J. H. H.; Hodgson, R.; Wagler, J.; Messerle, B. A. *Dalton Trans.* **2010**, *39*, 4062-4069.