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Supporting Information

# A Facile Solid-Phase Route to Renewable Aromatic Chemicals from Biobased Furanics

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# Supporting Information

## 1. Experimental Section

### 1.1. Synthesis of hydrogenated Diels-Alder (DA) adducts

All the hydrogenated DA adducts were prepared according to the method reported recently, see ref [9a] of main manuscript for details.

### 1.2. Zeolite materials

The zeolite catalysts used in this study were H-Beta ($SiO_2/Al_2O_3$=25, CP814E), H-Y ($SiO_2/Al_2O_3$=5.2, CBV600), H-VUSY ($SiO_2/Al_2O_3$=11.5, CBV712), and H-SDUSY ($SiO_2/Al_2O_3$=32.3, CBV700), which were all obtained from Zeolyst International. All zeolite materials were pretreated by heating them in air overnight at 550 $^oC$.

### 1.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the catalyst samples were obtained on a Bruker-AXS D2 Phaser powder X-ray diffractometer with Cu-Kα X-ray radiation (λ=1.5418 Å) operated at 30 kV and 10 mA. The textural properties of the samples were determined using a Micromeritics Tristar 3000 set-up. The $N_2$ adsorption and desorption experiments were conducted at 77 K after initial pre-treatment of the samples by degassing at 300 $^oC$ for 12 h under a $N_2$ flow. The surface area was determined using the Brunauer-Emmett-Teller (BET) method. The total pore volume was determined from the single point adsorption and the micropore volume was determined from the *t*-plot analysis. The pore size/diameter was derived from the adsorption isotherm by the Barrett-Joyner-Halenda (BJH) method. The acidity of the catalysts was evaluated using ammonia temperature-programmed desorption ($NH_3$-TPD) on a Micromeritics ASAP 2920 instrument. Typically, the sample (100 mg) was placed in a quartz reactor. The zeolite was dried in a He flow by heating with a temperature ramp of 5 $^oC\ min^{-1}$ to a maximum temperature of 600 $^oC$ to remove adsorbed water and chemisorbed species. Subsequently, the sample was cooled to 100 $^oC$ and $NH_3$ (10% in Ar) pulses were applied. The sample was then heated to 700 $^oC$ (5 $^oC\ min^{-1}$) to induce desorption of $NH_3$ under flowing He. The desorbed $NH_3$ was quantified using a TCD detector. The amount of ammonia desorbing at characteristic temperature above 100 $^oC$ is taken as the total concentration of acid sites. Thermal gravimetric analysis (TGA) of the catalysts was performed on a Perkin-Elmer Pyris 1 apparatus. The sample was initially heated to 50 $^oC$ for 10 min and then to 700 $^oC$ (10 $^oC\ min^{-1}$) in a 10 mL $min^{-1}$ flow of oxygen to burn off any carbonaceous deposits formed.

Selected trace metals (Fe, Zn, V, Ni, and Cu) in fresh, calcined zeolite Y samples were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Spectro Acros) after extraction with hydrofluoric acid.

### 1.4. Catalytic testing and regeneration

The catalytic performance of solid acid catalysts were tested using a Kugel-rohr glass oven (Buchi, B-585). In a typical reaction, 0.1 g of **2** and 0.1 g catalyst (1:1 wt%) were loaded in a round-bottom flask

and then mounted in the center of the preheated reactor. The mixture was stirred at 30 rpm under $N_2$ atmosphere. After the reaction, the solid acid catalyst was washed several times with chloroform at 45 $^oC$ and the catalyst was recovered by centrifugation. The combined organic extracts were evaporated under reduced pressure to obtain the crude products. Conversion and product yields were calculated[9a] from the $^1H$ NMR data (Varian 400-MR spectrometer) of the crude mixture using $CDCl_3$ (99.8 atom%, Sigma-Aldrich) and 1,4-dinitrobenzene (99%, Sigma-Aldrich) as solvent and internal standard, respectively. Catalyst regeneration of H-Y catalyst was performed by drying the spent catalyst overnight at 60 $^oC$ followed by 120 $^oC$ for 2 h, and finally at 550 $^oC$ for 6 h in air to again obtain a white-colored material.


**Figure S1**. Photograph of Kugelrohr vessel filled with substrate and zeolite.

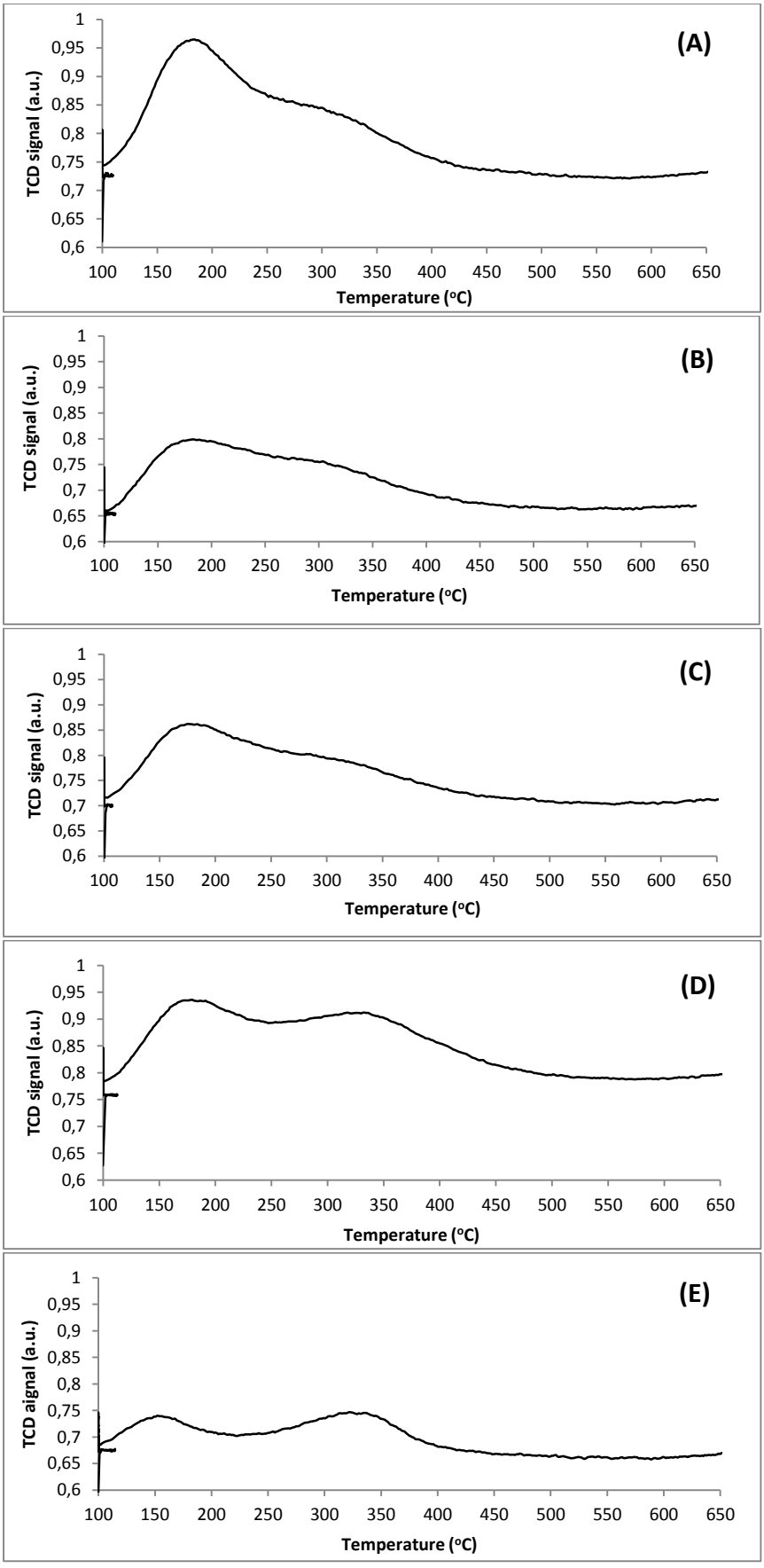



**Figure S2**. $NH_3$-TPD profiles of the catalysts: (A) H-Beta, (B) H-Y (fresh) , (C) H-Y (after 3rd reuse), (D) H-VUSY, and (E) H-SDUSY.

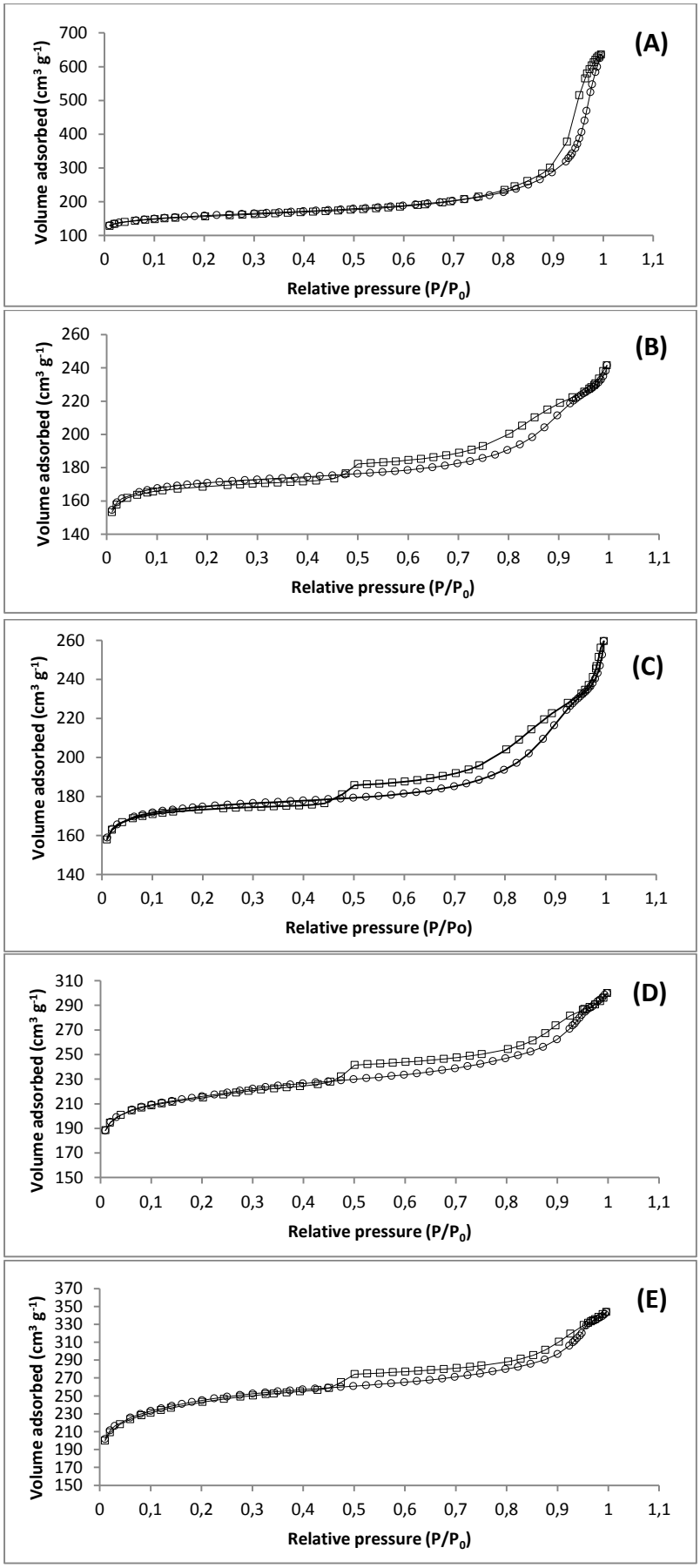



**Figure S3**. $N_2$ adsorption (circles) and desorption (squares) isotherms of the catalysts: (A) H-Beta, (B) H-Y (fresh), (C) H-Y (after 3rd reuse), (D) H-VUSY, and (E) H-SDUSY.

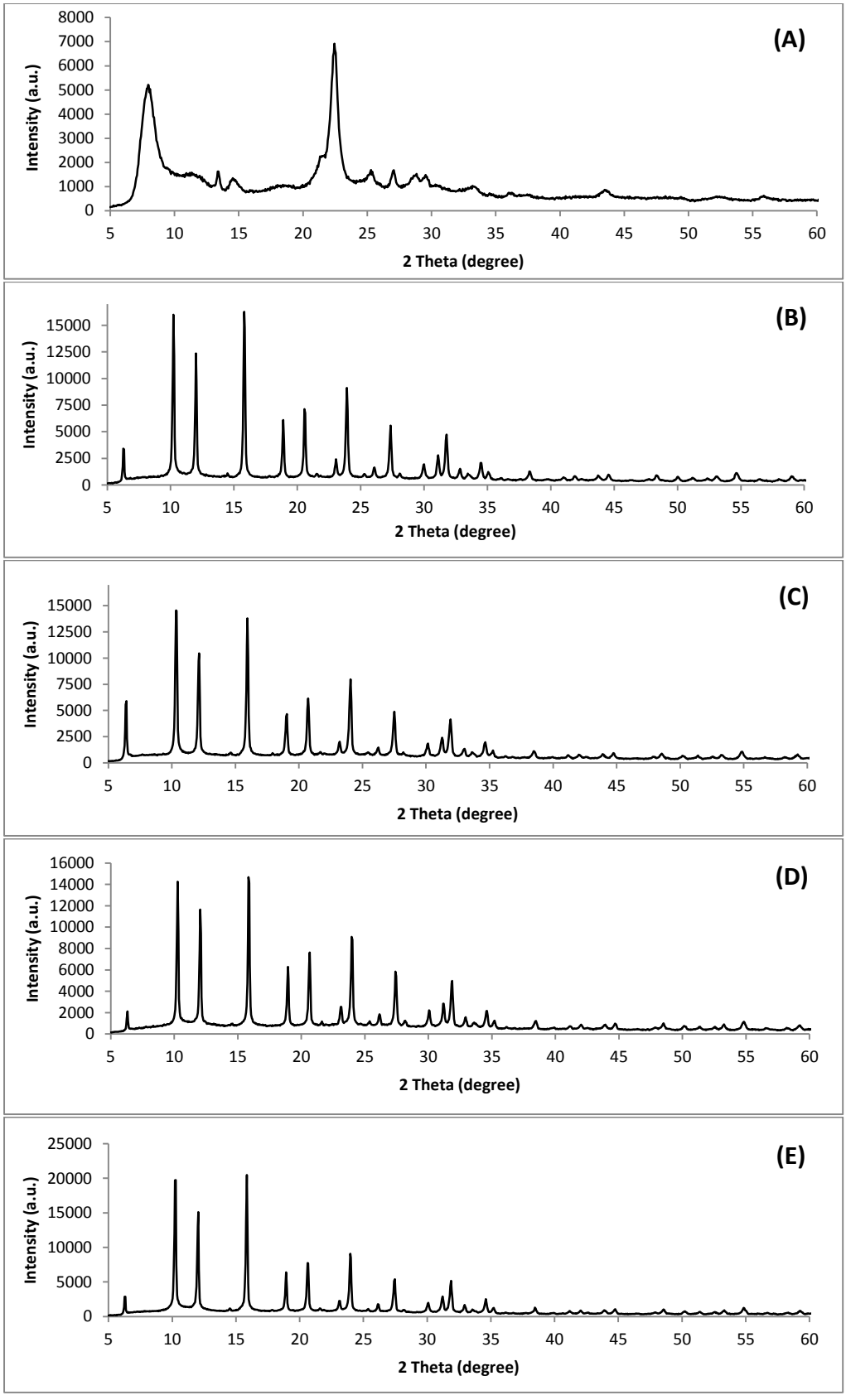



**Figure S4.** XRD patterns of the catalysts: (A) H-Beta, (B) H-Y (fresh), (C) H-Y (after 3rd reuse), (D) H-VUSY, and (E) H-SDUSY.

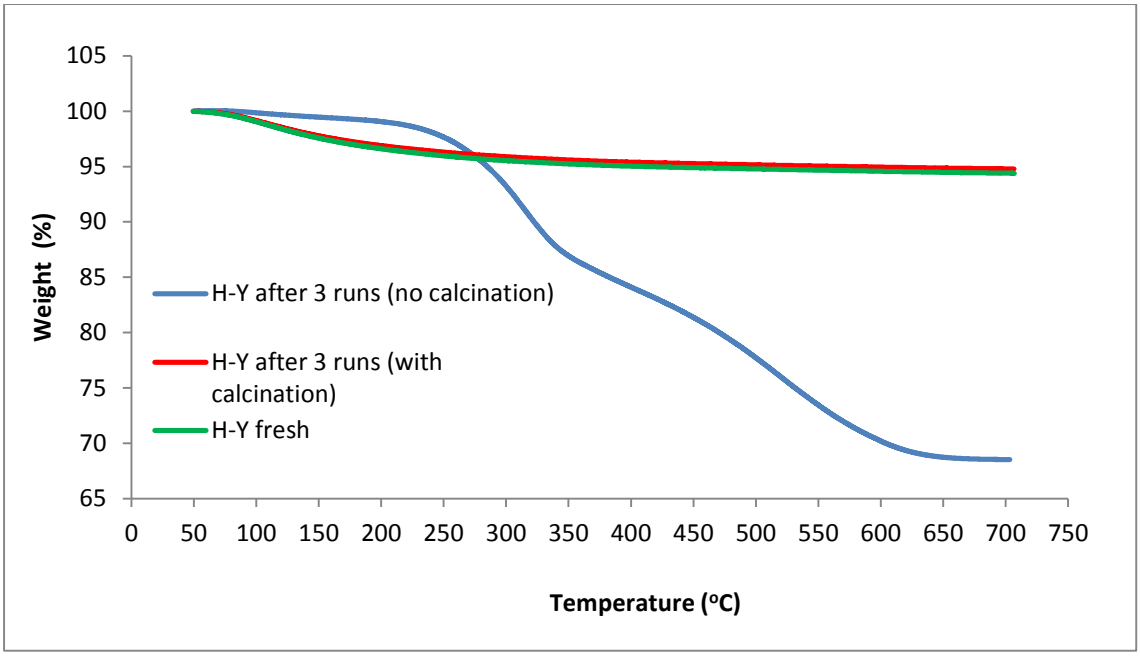
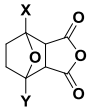
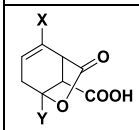
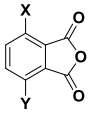
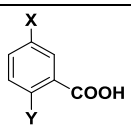
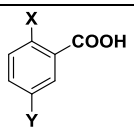
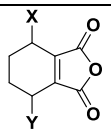



**Figure S5.** TGA profiles of fresh, spent (after 3rd reuse), and regenerated (calcined, after 3rd reuse) H-Y catalysts.

**Table S1.** Concentration (mg $kg^{-1}$) of selected trace metals in commercial zeolite Y samples analyzed by ICP-AES.

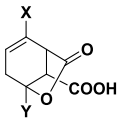
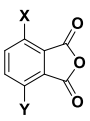
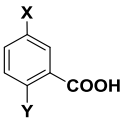
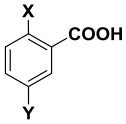
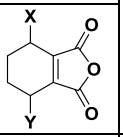
| Zeolite Y | Cu | Fe | Ni | V | Zn |
|---|---|---|---|---|---|
| H-Y | 20 | 101 | 2 | < -0.4 | 18 |
| H-VUSY | 14 | 75 | 1 | < -0.4 | 10 |
| H-SDUSY | < -1.3 | 90 | 2 | < -0.5 | 8 |

**Table S2.** Catalytic aromatization of hydrogenated Diels-Alder adducts in the solid-phase route using H-Y catalyst at 50% (w/w) catalyst loading.[a]

| Temp. (°C) |  | Conversion (mol %)[b] | Molar yield [mol %] (Selectivity [mol %])[b]  |  |  |  |  | Mole balance[c] |
|---|---|---|---|---|---|---|---|---|
| 150 | X=$CH_3$; Y=H | 97 | 59 [61] | 17 [17] | 2 [2] | -[d] | -[d] | 81 |
| 175 | X=$CH_3$; Y=H | 98 | 42 [43] | 32 [32] | 6 [6] | -[d] | 2 [2] | 84 |
| 200 | X=$CH_3$; Y=H | 88 | 16 [18] | 37 [43] | 8 [9] | 3 [4] | 4 [4] | 80 |

[a] Conditions: 0.1 g of **2**, 0.05 g solid acid catalyst, 120 min. [b] Calculated by q-NMR using 1,4-dinitrobenzene as internal standard. [c] Mole balance determined from the total number of moles calculated from the crude mixture after the reaction by $^1$H-NMR analysis. [d] Not observed.

**Table S3.** Aromatization of hydrogenated Diels-Alder adduct **2** and product yields as a function of time at 200 °C over H-Y at 1:1 w/w ratio.[a]

| Time (min) | Conversion (mol %)[b] | Molar yield [mol %] | | | | | Total aromatics yield (4+5+6, %) | Mole balance[c] |
|---|---|---|---|---|---|---|---|---|
| | |  |  |  |  |  | | |
| 5 | 100 | 59 | 16 | 9 | 5 | 4 | 30 | 93 |
| 15 | 100 | 42 | 21 | 14 | 5 | 5 | 40 | 87 |
| 30 | 97 | 10 | 46 | 13 | 5 | 6 | 64 | 83 |
| 60 | 100 | 8 | 47 | 14 | 8 | 5 | 69 | 82 |
| 90 | 100 | 6 | 51 | 13 | 7 | 6 | 71 | 83 |
| 120 | 100 | 0 | 61 | 12 | 7 | 6 | 80 | 86 |

[a] Conditions: 0.1 g of **2**, 0.1 g solid acid catalyst, [b] Calculated by q-NMR using 1,4-dinitrobenzene as internal standard. [c] Mole balance determined from the total number of moles calculated from the crude mixture after the reaction by $^{1}$H-NMR analysis.

**Movie S1.** Solid-phase aromatization of hydrogenated Diels-Alder adduct in Kugelrohr oven in the presence of H-Y zeolite (1:1 wt%) as catalyst - in action.

**Movie S2.** $H_2$ in the aromatization of hydrogenated Diels-Alder was detected using a $H_2$ detector (LC10) - in action.