# Supporting Information

## Covalent triazine framework @ silica core-shell spheres decorated with ultrafine platinum nanoparticles: a robust catalyst for selective aqueous phase hydrogenation of butane-2,3-dione and pyruvic acid

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## 1. Synthesis

### 1.1. Synthesis of terephthalamidine dihydrochloride

According to a previously reported synthesis [see ref. 27 of the manuscript], a 100 mL 3-neck round bottom flask equipped with a magnetic stir bar and dropping funnel was charged under Ar with 0.641 g of terephthalonitrile (5.00 mmol, Merck 98.0%) and 20 mL of anhydrous THF. The flask was placed in an ice-water bath and 20 mL of 0.5 M $LiN(SiMe_3)_2$ in 2-methyltetrahydrofuran (26 mmol, 5.2 equiv.) was added dropwise over 30 min. The bath was removed, obtaining a clear orange solution that was left stirring for 3 hours at 25°C before being cooled at 0°C and then quenched by careful addition of 20 mL of 6 M HCl-EtOH. After 18 h the suspension was filtered and washed with diethyl ether, obtaining 1.5 mg of crude terephthalamidine dihydrochloride.

The product thus obtained was purified by recrystallization from $H_2O$-EtOH (1:5). The crystals were filtered under vacuum on a sintered glass frit and dried at reduced pressure, to give 0.823 g (3.50 mmol, 70 % yield) of the title compound.

$^1H$ NMR (400 MHz, $D_2O$): δ (ppm) = 7.82 (s, 4H, aromatic H), 4.64 (s, 8H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, $D_2O$): δ (ppm) = 165.86, 132.9, 128.7.

## 2. Figures

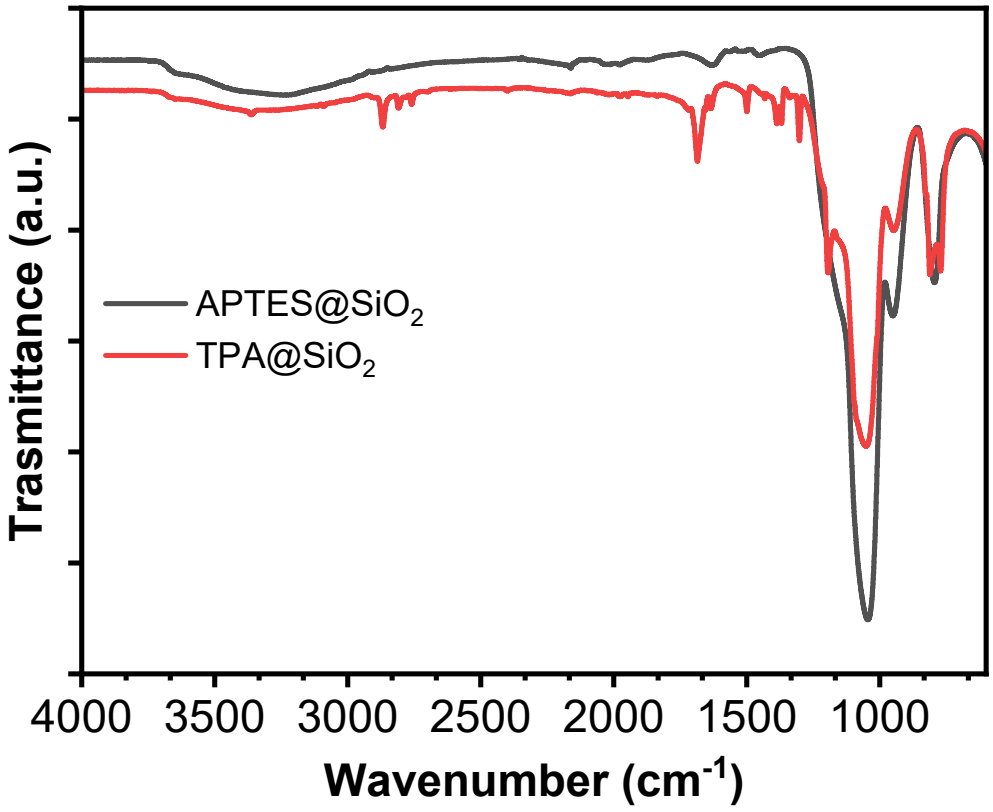



**Fig. S1.** FT-IR spectra of APTES@$SiO_2$ (grey) and TPA@$SiO_2$ (red).

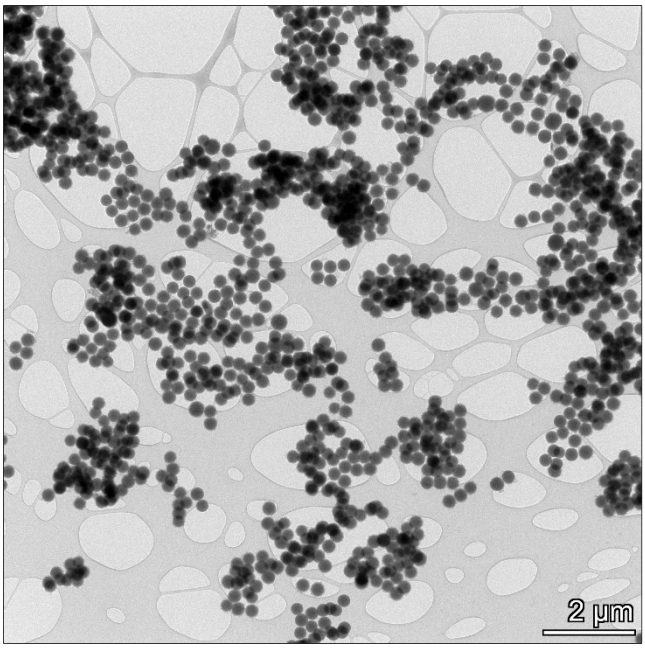



**Fig. S2.** Representative low magnification TEM micrograph of CTF@$SiO_2$.

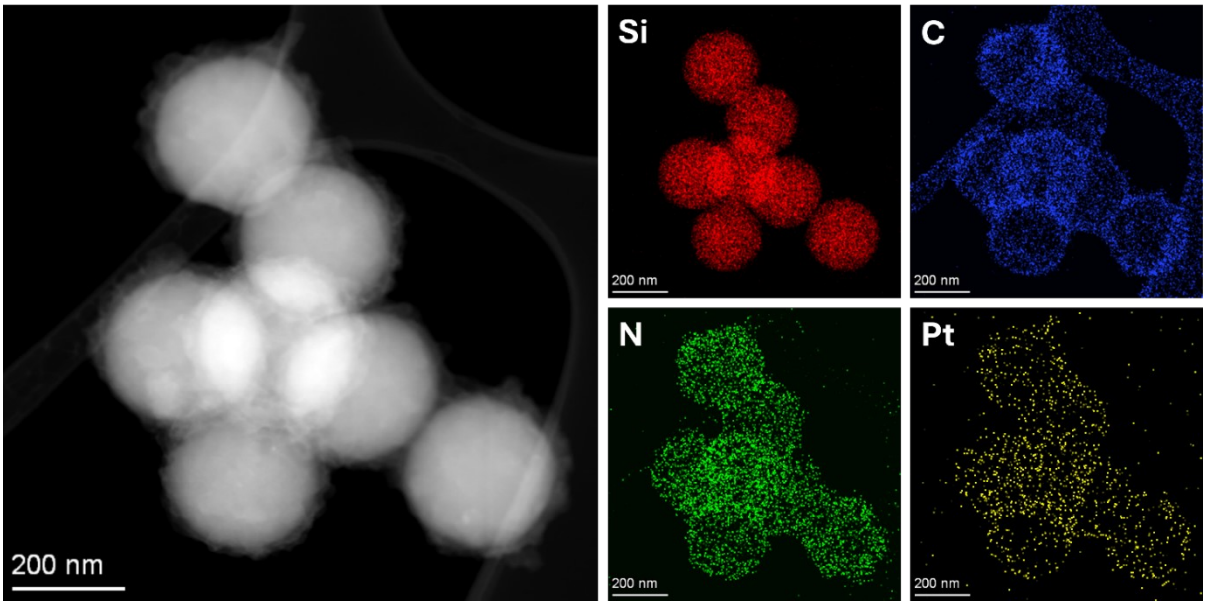



**Fig. S3**. HAADF-STEM/EDS element map of Pt/CTF@$SiO_2$.

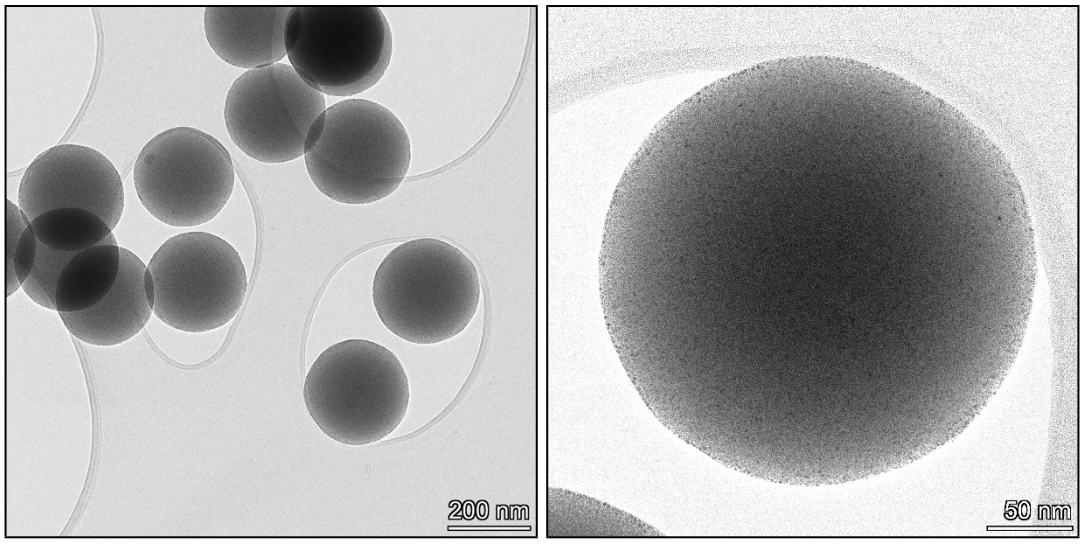



**Fig. S4.** Representative TEM micrographs of $Pt/SiO_2$.

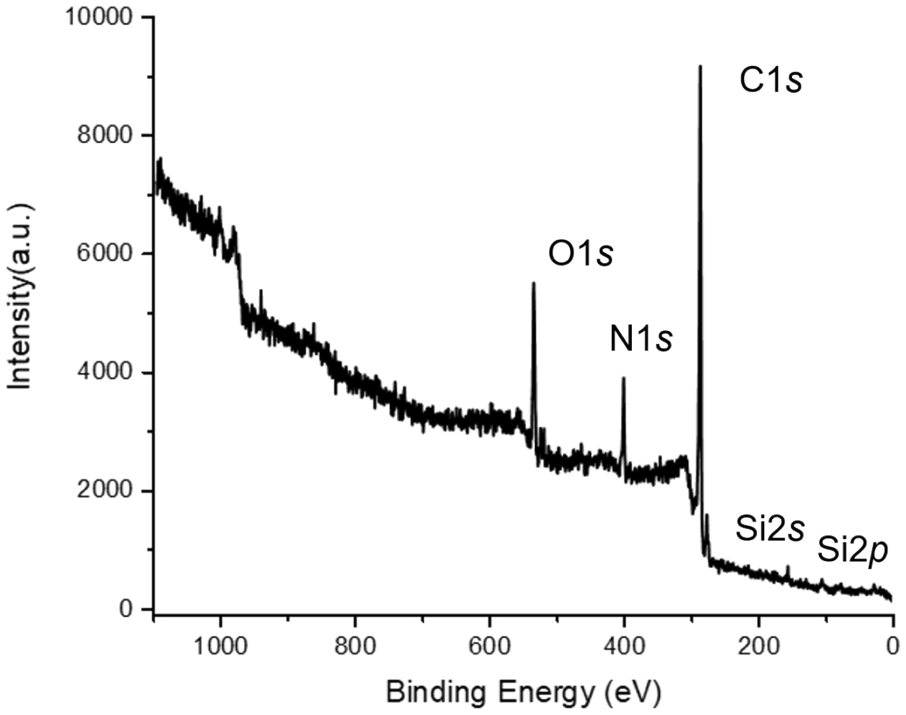



**Fig. S5.** Survey XPS spectrum for $CTF@SiO_2$.

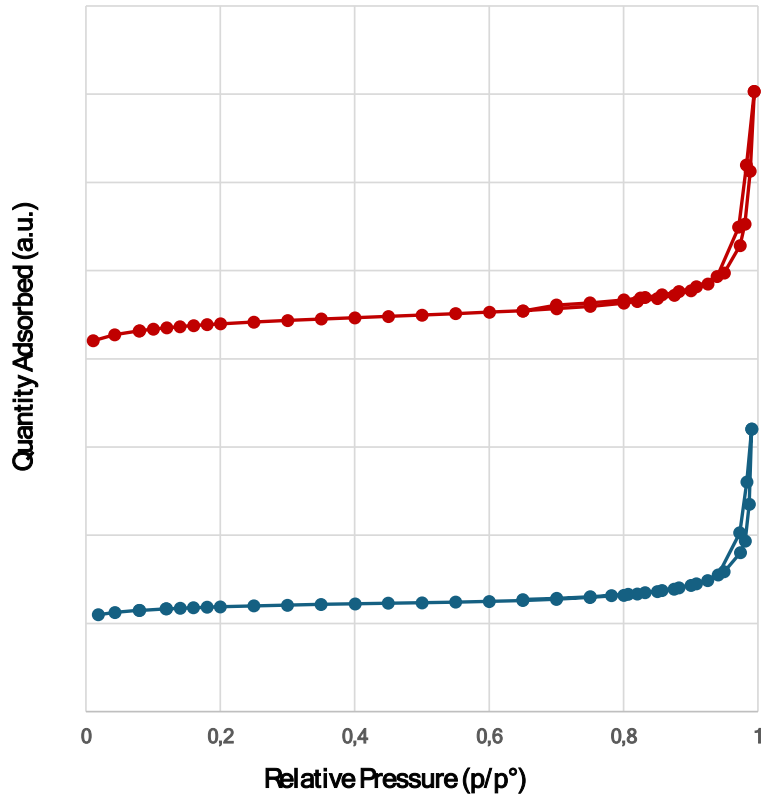



**Fig S6.** Nitrogen physisorption isotherms for $SiO_2$ (upper) and CTF@$SiO_2$ (lower).

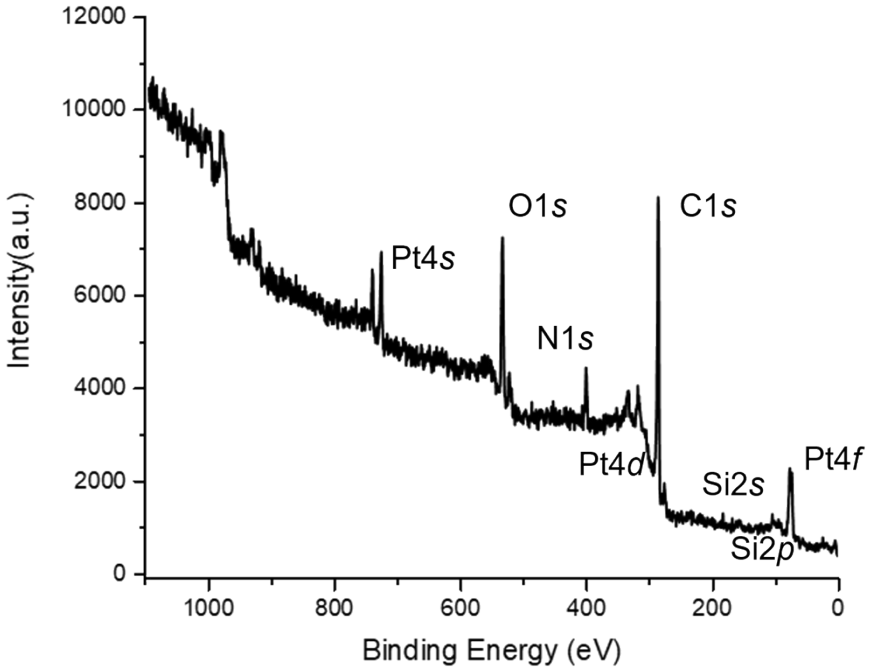



**Fig. S7.** Survey XPS spectrum for **1.**

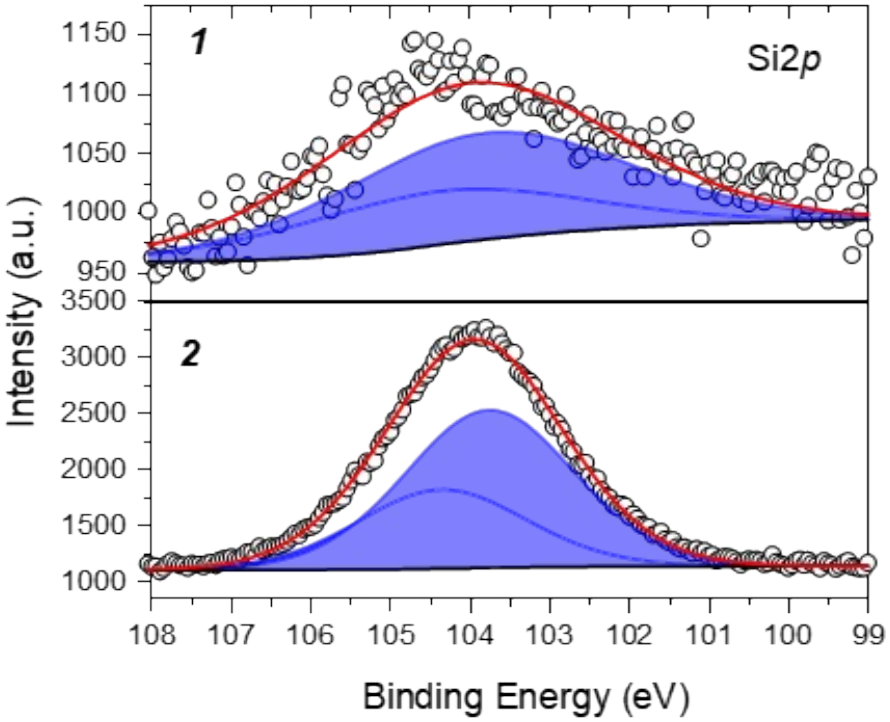



**Fig. S8. Si2*p*** XPS spectra for **1** and **2**.

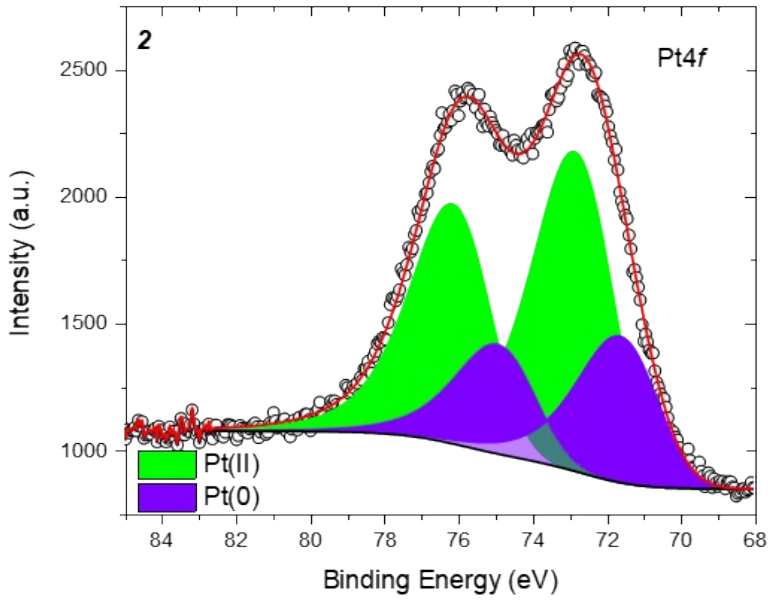



**Fig. S9.** Pt4*f* XPS spectrum for **2**.

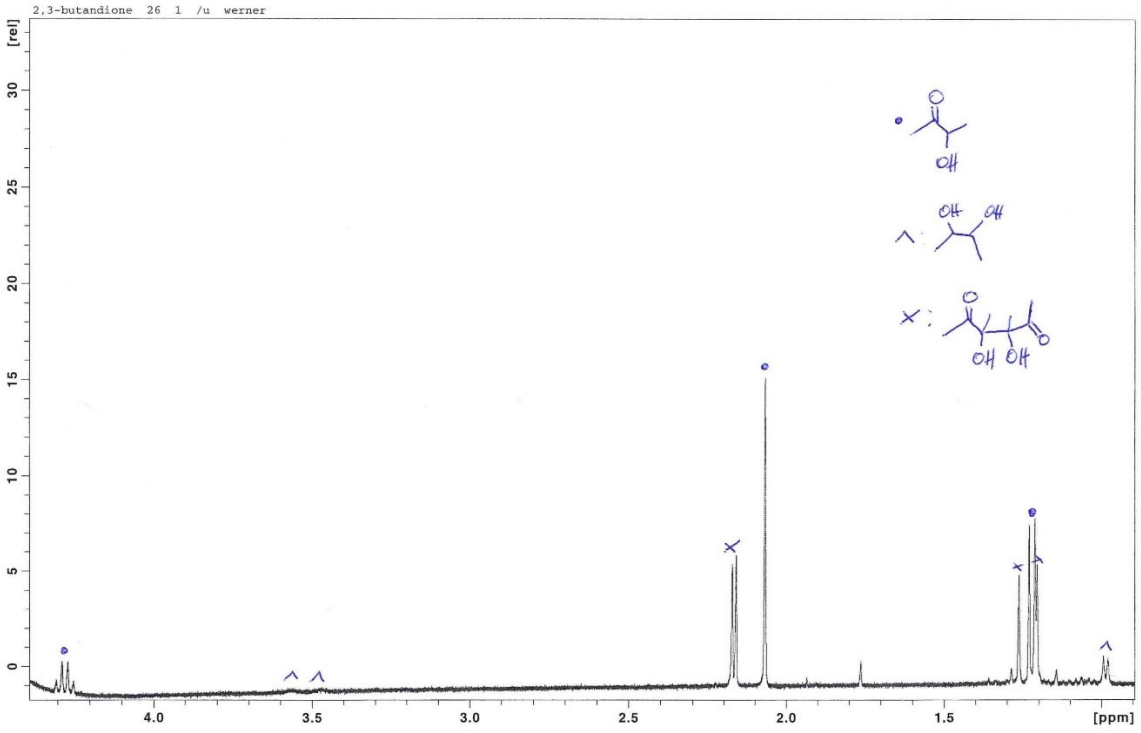



**Fig. S10.** $^{1}H$ NMR spectrum acquired with an Evans tube ($D_2O$) for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 85 °C for half an hour.

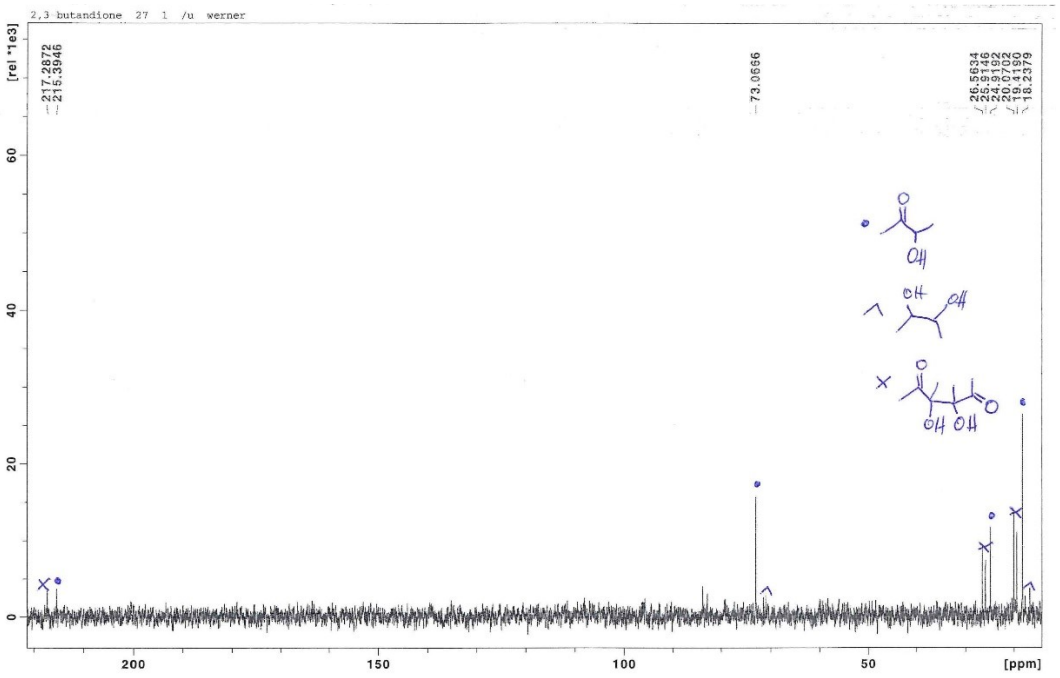



**Fig. S11.** $^{13}C\{^{1}H\}$ NMR spectrum acquired with an Evans tube ($D_2O$) for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 85 °C for half an hour.

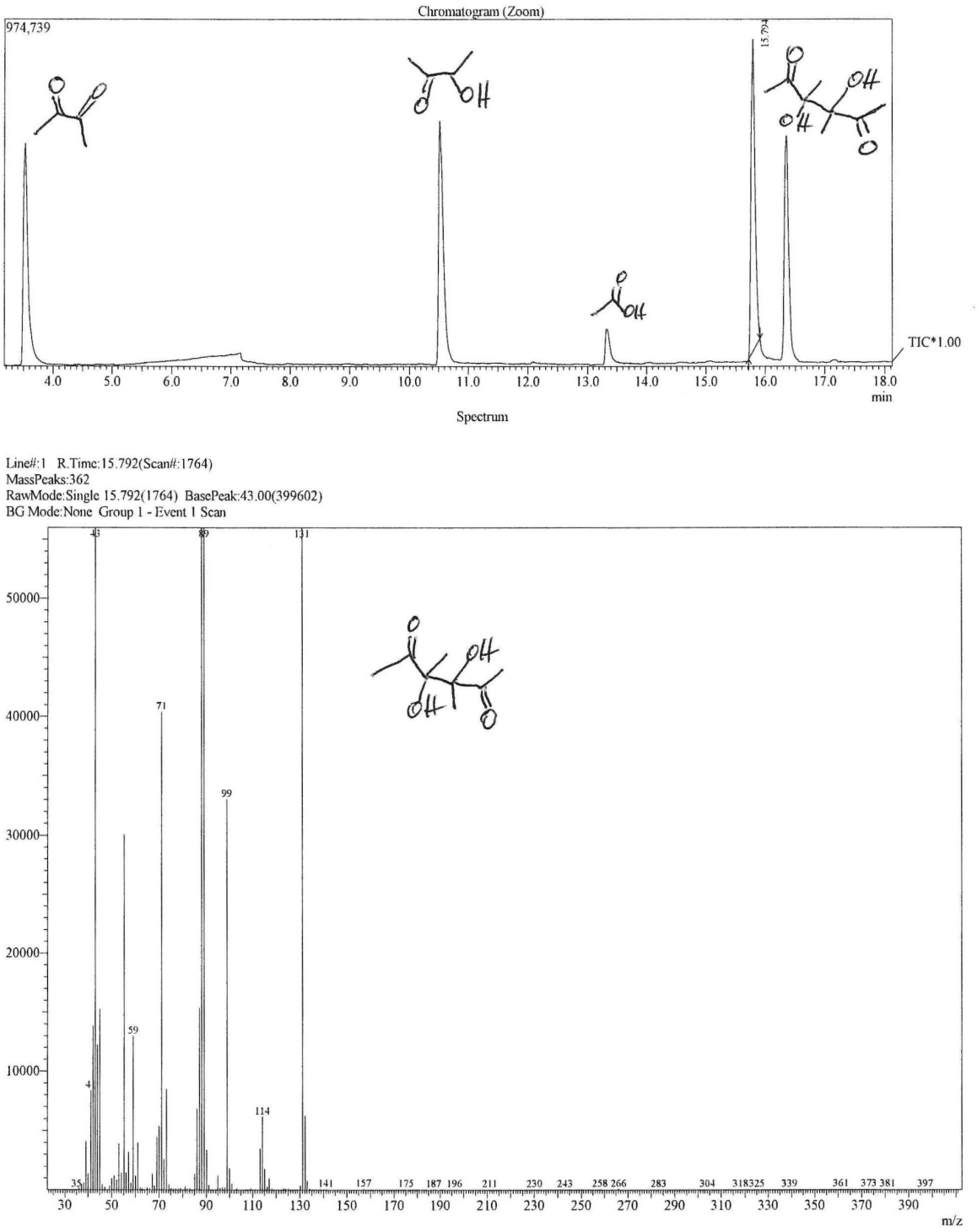



**Fig. S12.** GC trace for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 85 °C for 3 h (top) and MS spectrum for 3,4-dihydroxy-3,4-dimethylhexa-2,5-dione (bottom).

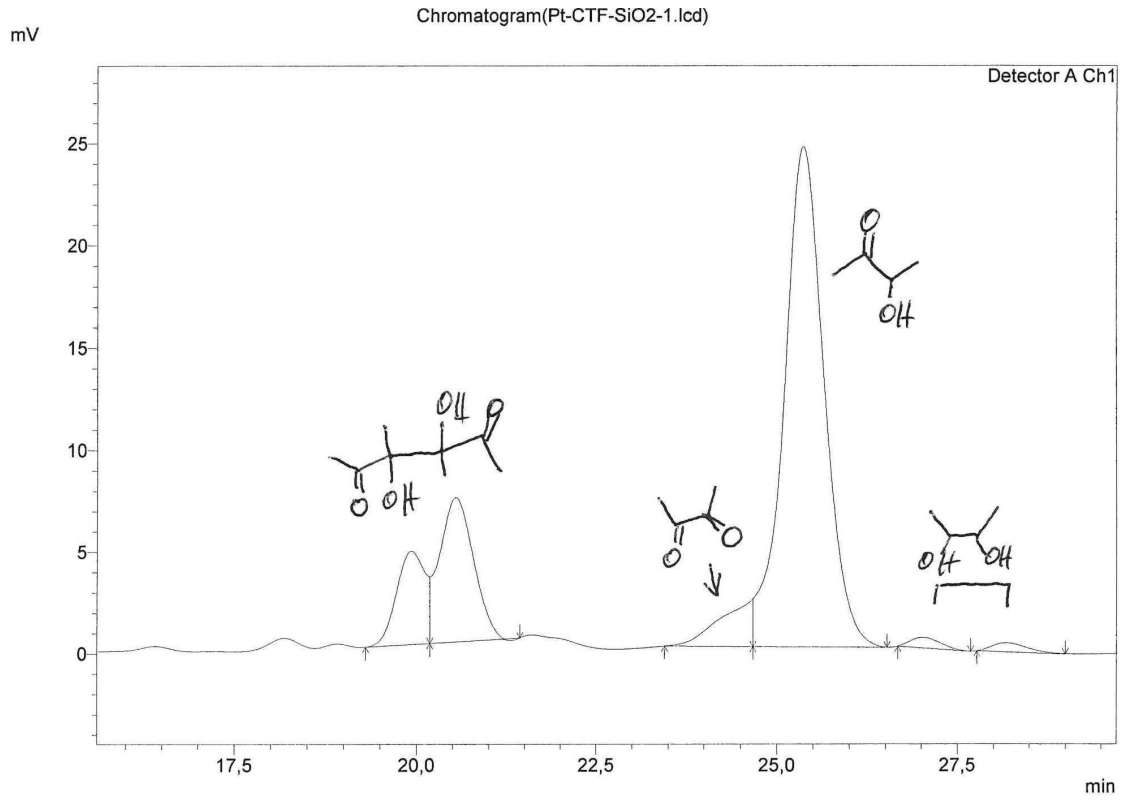



**Fig. S13**. HPLC trace for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 85 °C for 3 h.

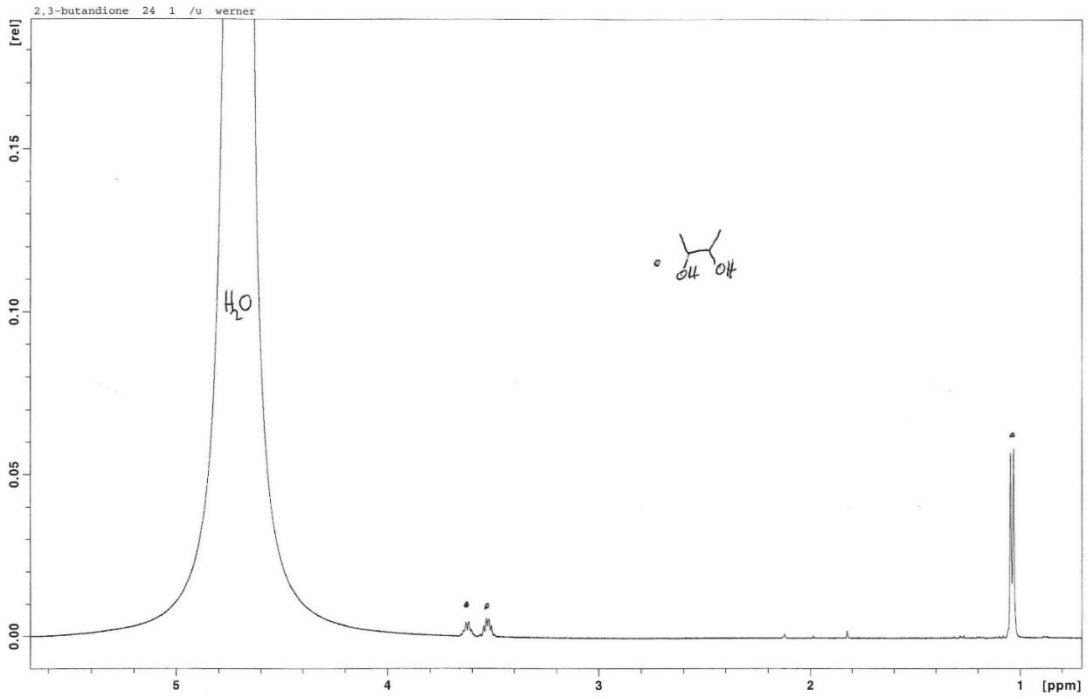



**Fig. S14.** $^{1}$H NMR acquired with an Evans tube ($D_2O$) for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 105 °C for 15 h.

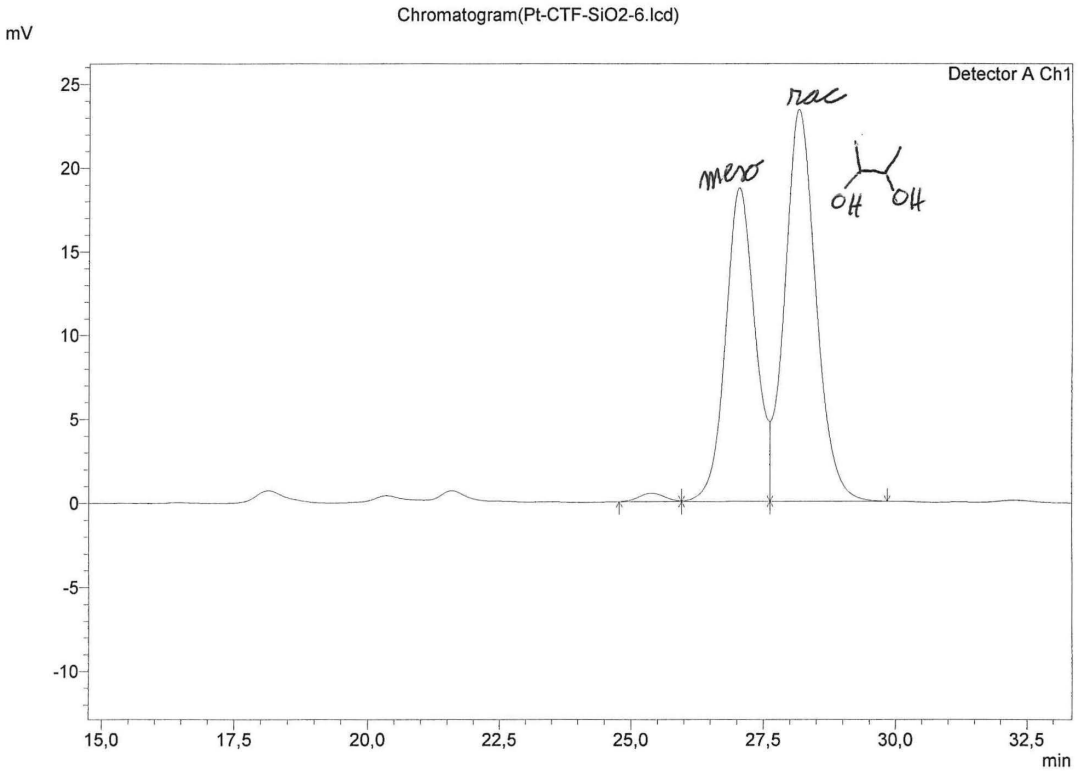
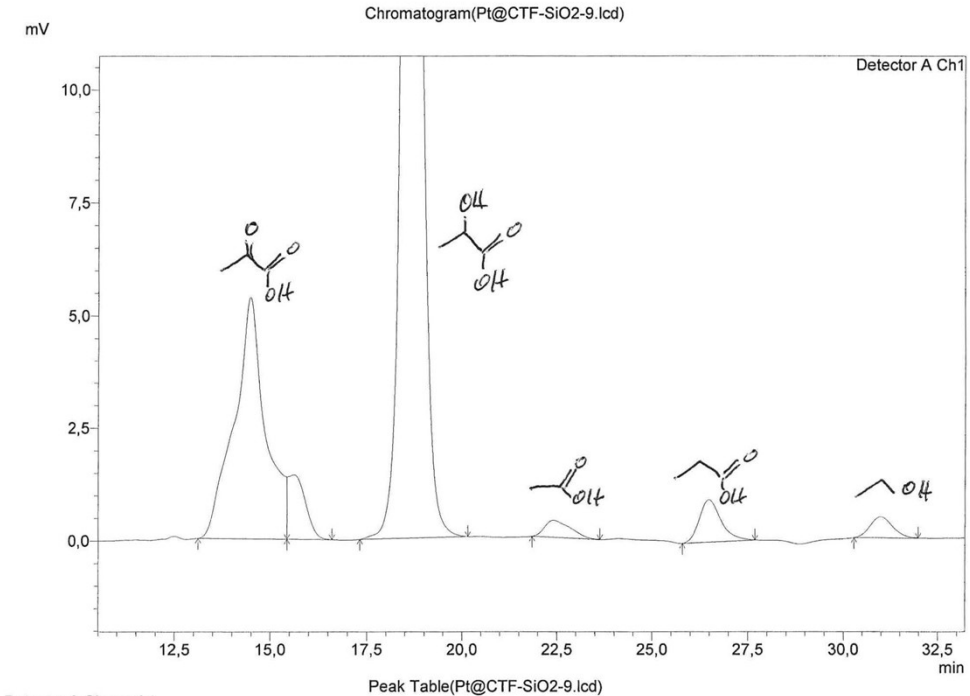



**Fig. S15.** HPLC trace for the **1**-catalyzed 2,3-BDO hydrogenation carried out at 105 °C for 15 h.




Peak Table(Pt@CTF-SiO2-9.lcd)

Detector A Channel 1

| Peak# | Ret. Time | Area | Conc. | Name | Area% |
|---|---|---|---|---|---|
| 1 | 14.479 | 306500 | 0.000 | | 19.259 |
| 2 | 15.622 | 44618 | 0.000 | | 2.804 |
| 3 | 18.643 | 1165835 | 0.000 | | 73.256 |
| 4 | 22.404 | 17779 | 0.000 | | 1.117 |
| 5 | 26.491 | 37569 | 0.000 | Propionic | 2.361 |
| 6 | 30.982 | 19152 | 0.000 | EtOH | 1.203 |
| Total | | 1591453 | 0.000 | | 100.000 |

**Fig. S16**. HPLC trace for the **1**-catalyzed pyruvic acid hydrogenation at 105 °C for 1 h.

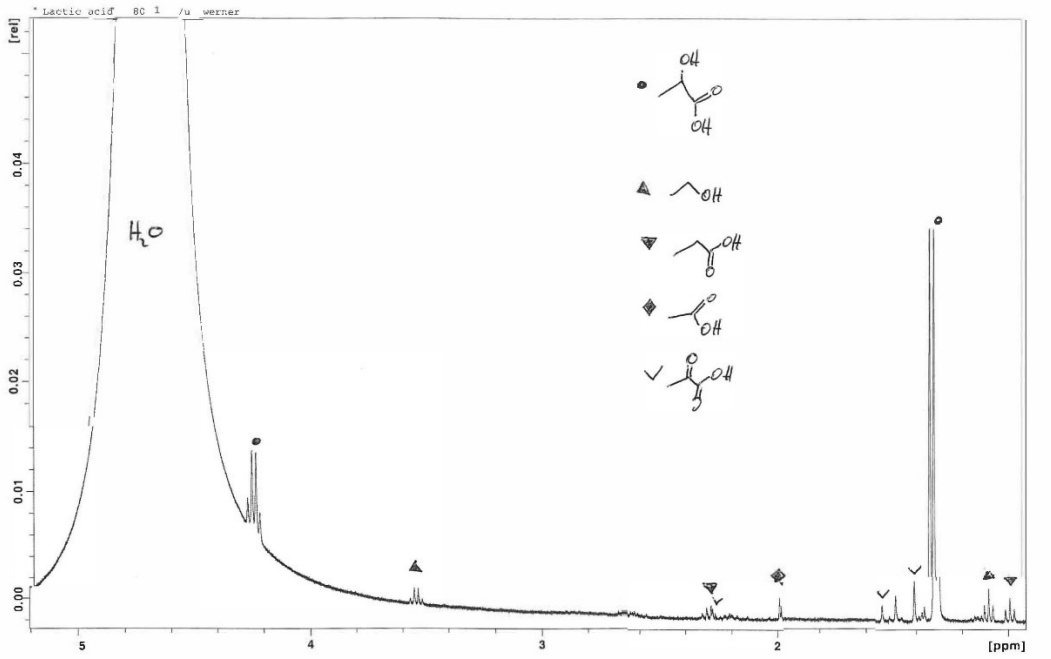



**Fig. S17**. $^{1}$H NMR spectrum for the **1**-catalyzed pyruvic acid hydrogenation carried out at 105 °C for 1 h.

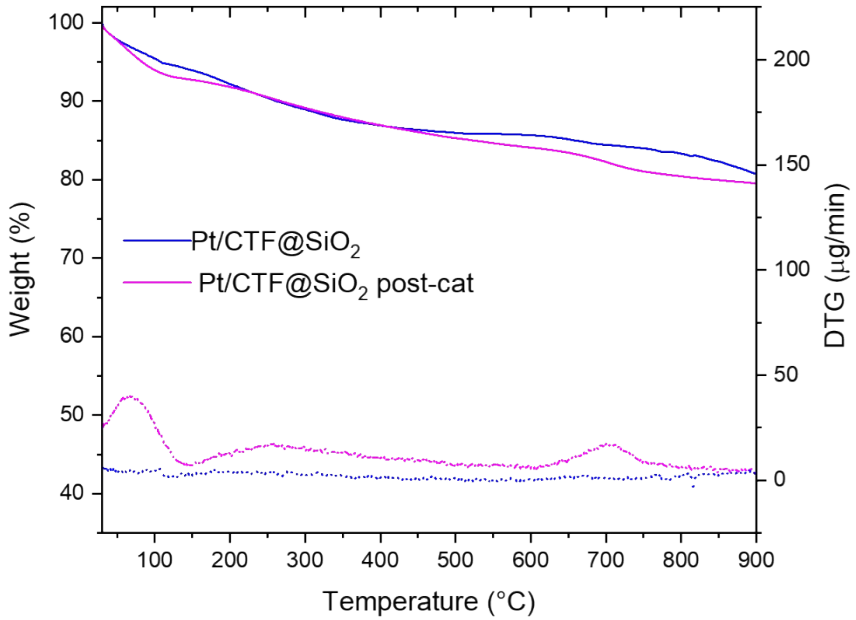



**Fig. S18**. TGA analysis under a nitrogen atmosphere (200 mL/min) from 30°C to 900°C at a heating rate of 10°C/min of as-synthesized **1** (blue) and recovered **1** after four catalytic cycles (violet), Table 1 entry 15.

## 3. Tables

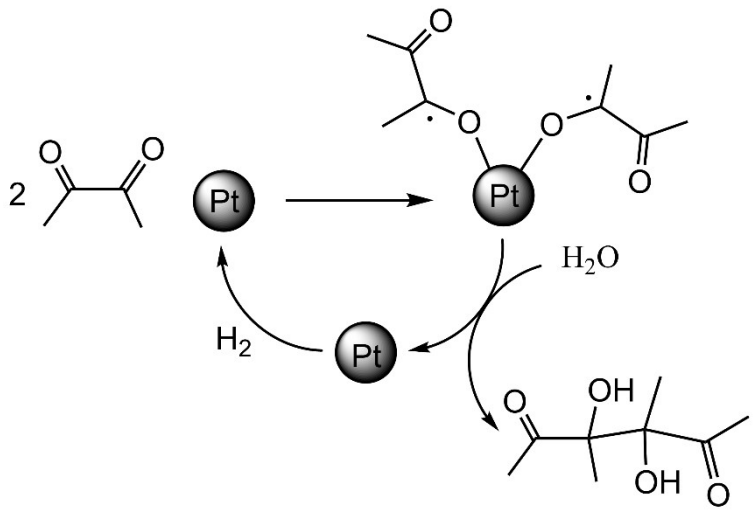
**Table S1**. Binding energies (B.E.) for Si2$p_{3/2}$, N1$s$ and Pt4$f_{7/2}$ given in eV.

| Sample | B.E. Si2$p_{3/2}$ (eV) | B.E.N1$s$ (eV) | B.E. Pt4$f_{7/2}$ (eV) |
|---|---|---|---|
| CTF@$SiO_2$ | 103.7 | 399.0, 400.6, 402.5 | - |
| **1** | 103.9 | 399.1, 400.6, 402.5 | 71.1 [Pt(0), 16.7%] |
| | | | 72.3 [Pt(II), 83.3%] |
| **2** | 103.7 | - | 71.0 [Pt(0), 31.5%] |
| | | | 72.3 [Pt(II), 68.5%] |

**Table S2**. Specific Surface Area (SSA) for $SiO_2$ and CTF@$SiO_2$.

| Sample | SSA($m^2$/g) |
|---|---|
| $SiO_2$ | 16 |
| CTF@$SiO_2$ | 33 |

## 4. Scheme




**Scheme S1**. Proposed catalytic cycle for the Pt-NP-catalyzed reductive coupling of 2,3-BDO in the presence of hydrogen and water.