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# Chiral crystalline organic salts as supports of Pd nanoparticles forming selective heterogeneous catalysts for hydrogenation of nitroarenes

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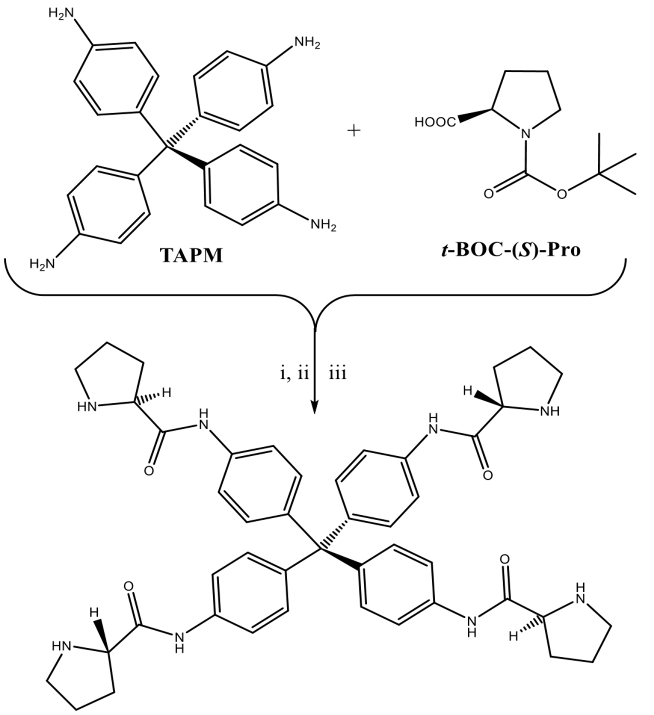
In this work we report the synthesis of a chiral tecton **(*S*)-TPPM** (Scheme S1), its reaction with tetrasodium tetrakis(4-sulfonatophenyl)methane (**TSPM**) to give a crystalline organic porous salts (CPOS) **CF2,** then a Pd entrapped heterogeneous catalyst **Pd@CF2** (Scheme S1) and its performance as a catalyst of hydrogenation of nitroaromatics.



(2*S*,2'*S*,2''*S*,2'''*S*)-*N*,*N*',*N*'',*N*'''-(methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(pyrrolidine-2-carboxamide)

**TPPM**

**Scheme S1.** Reagents and conditions: i $CH_2Cl_2$, N,N'-dicyclohexylcarbodiimide, ii $CF_3COOH$, iii KOH, $H_2O$

The CPOS entrapped palladium nanoparticles (**Pd@CF2**) were prepared in a three-step procedure (see Scheme 1 of the main text). Firstly, an aqueous solution of an equivalent of tetrasodium tetrakis(4-sulfonatophenyl)methane **TSPM** and two equivalents of insoluble palladium(II) dichloride were mixed at a room temperature and the agitation was continued until all $PdCl_2$ dissolved to give the corresponding soluble Pd salt of **TSPM**. Then one equivalent of insoluble **TPPM** was added, and the mixture was stirred for 24 hours after which the flask was evacuated, filled with $H_2$, and the mixture was stirred under a hydrogen atmosphere at ambient temperature for 24 hours to give **Pd@CF2** as a black precipitate. The elemental analysis of the black powder corresponded to the formula $C_{140}H_{144}N_{16}O_{32}Pd_5S_8 \times 27(H_2O)$, showing that it contained up to 13% of palladium by weight.

*Scanning transmission electron microscopy (STEM) of* ***Pd@CF2*** *after catalytic hydrogenation.* For the STEM measurements, the sample was deposited on the surface of carboncoated copper TEM grid (200 mesh) from suspension in tetrahydrofuran. The observations were carried out using Hitachi Regulus8230 (SU8230) field-emission scanning electron microscope (FE-SEM). Images were acquired in transmitted electron mode (bright-field STEM mode) at a 30 kV accelerating voltage.

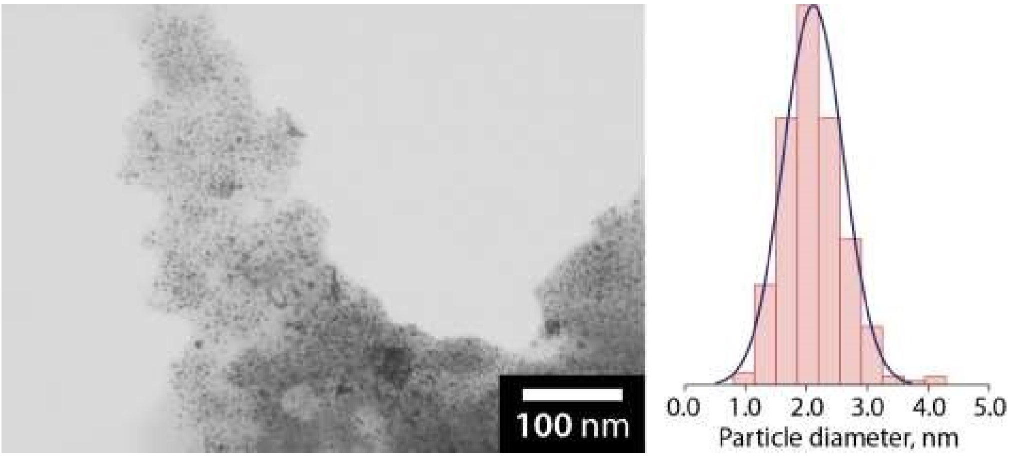
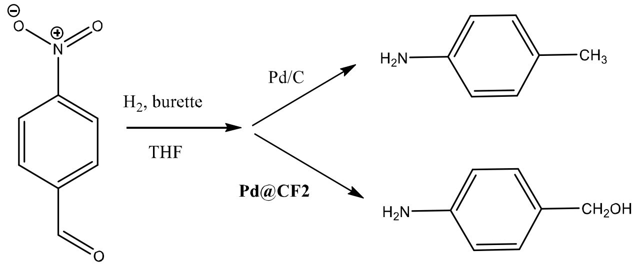


**Figure S1.** Representative BF-STEM image of **Pd@CF2** isolated from the reaction mixture for the catalytic hydrogenation as well as the corresponding palladium particle diameter distribution.

The substrate *p*-nitrobenzaldehyde **3** was reduced to *p*-aminotoluene **5** (Figures S2, S3) with $H_2$ on Pd/C and to *p*-aminobenzyl alcohol **4** (Figures S4-S6) if promoted with **Pd@CF2** according to MS and $^1$H NMR data.

Figure 2 (main text) illustrates the kinetic curves of the reductions.



**Scheme S2.**

**4-aminotoluene (5)**[S1] The reduction of 4-nitrobenzaldehyde promoted by Pd/C (THF) gives 4-aminotoluene **(5)** in a quantitative yield .$^1$H NMR (400 MHz, $CDCl_3$) δ: 7.01 (d, *J*=8,3 Hz, 2H); 6.65 (d, *J*=8,3 Hz, 2H), 3.53 (br.s, 2H), 2.28 (s, 3H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 144,0, 129.8, 127.7, 115.3, 20.6 ppm. HRMS (ESI): found m/z 108.0807; calculated for $C_7H_9N$ $[M+H]^+$ 108.0808.

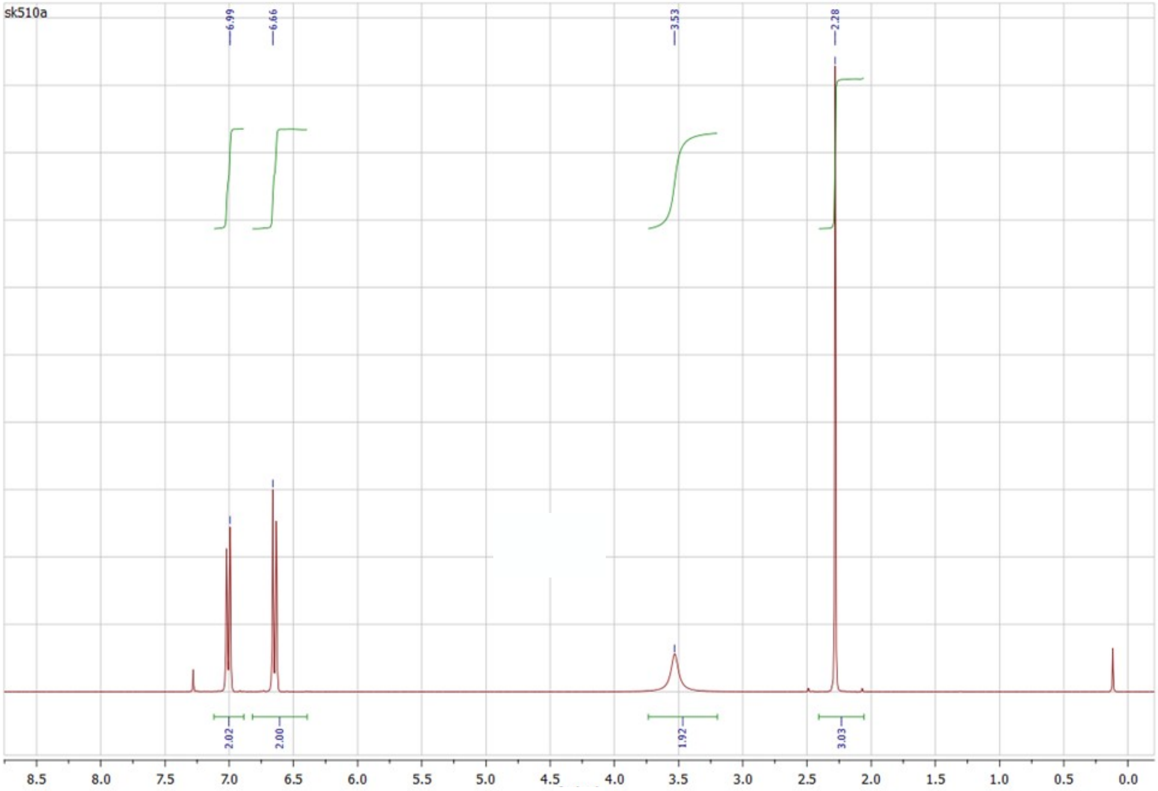


**Figure S2.** $^1$H NMR spectrum of ***p*-aminotoluene (5)**.

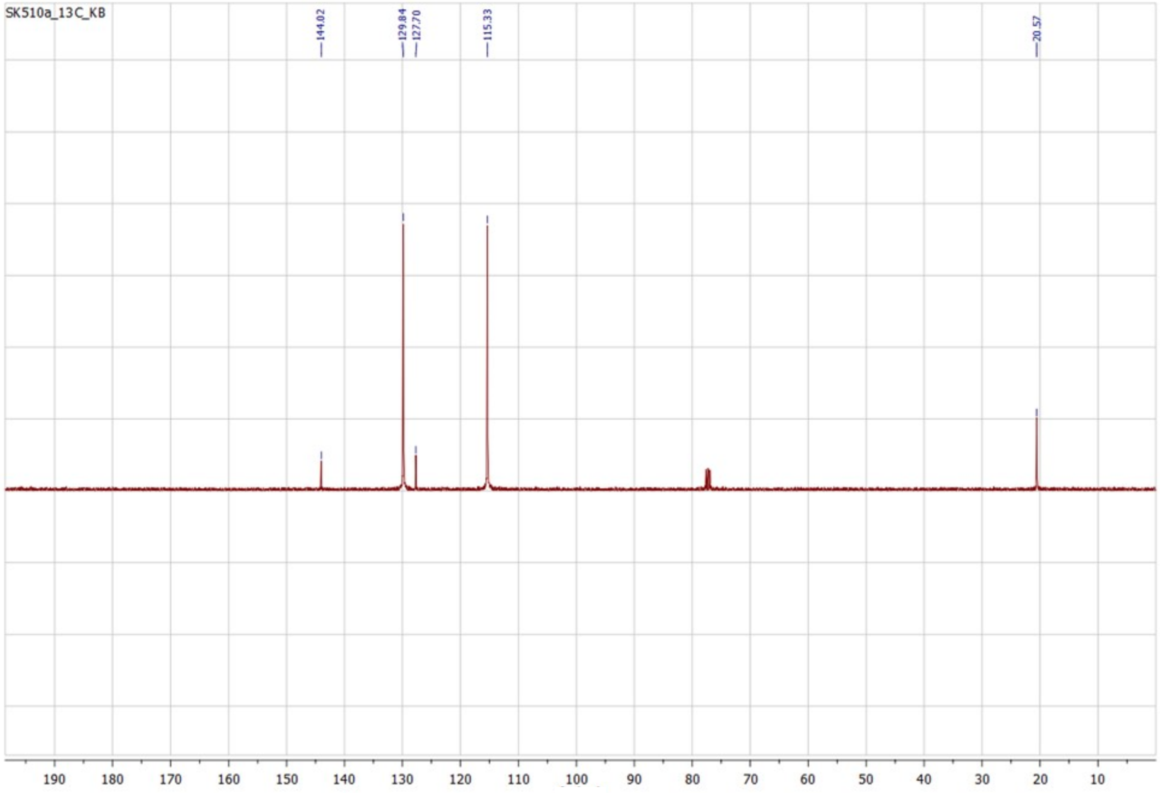


**Figure S3.** $^{13}$C NMR spectrum of ***p*-aminotoluene (5).**

**4-aminobenzyl alcohol (4)**[S2]. The reduction of 4-nitrobenzaldehyde **(3)** promoted by Pd@CF$_2$ (THF) gives a mixture of **4-aminobenzyl alcohol (4)** and an admixture of (4-((4-aminobenzylidene)amino)phenyl)methanol (Figure S4).

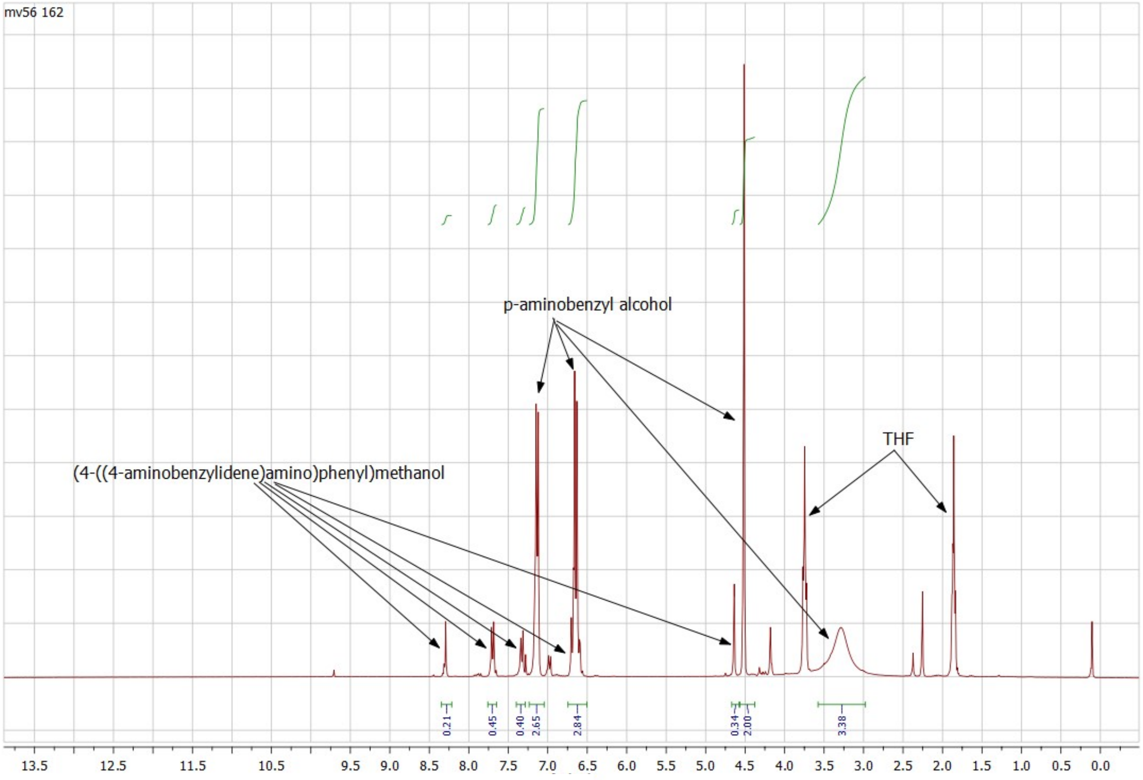


**Figure S4**. $^1$H NMR spectrum of the reaction mixture of the reduction of 4-nitrobenzaldehyde promoted by Pd@$CF_2$.

Purification by column chromatography (silica, elution with ethyl acetate : petroleum ether 3:1) gave ***p*-aminobenzyl alcohol (4)** as a colorless liquid (0.22 g, 1.8 mmol, 45%). $^1$H NMR (400 MHz, $CDCl_3$) δ: 7.14 (d, *J=8,2* Hz, 2H); 6.65 (d, *J=8,2* Hz, 2H), 4.53 (s, 2H), 3.55 (br.s, 2H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ: 145.8, 131.2, 128.7, 115.2, 64.8 ppm. HRMS (ESI): found m/z 124.0755; calculated for $C_7H_{10}NO$ $[M+H]^+$ 124.0757.

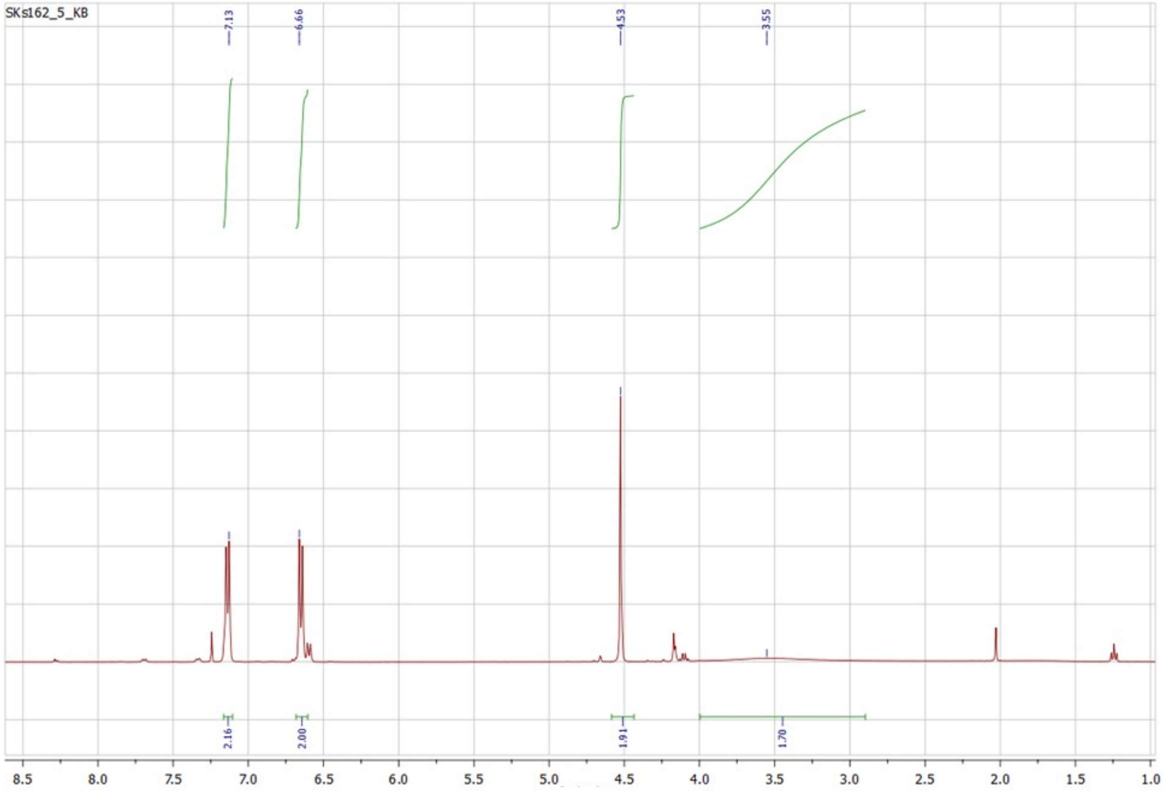


**Figure S5.** $^1$H NMR spectrum of ***p*-aminobenzyl alcohol (4)**

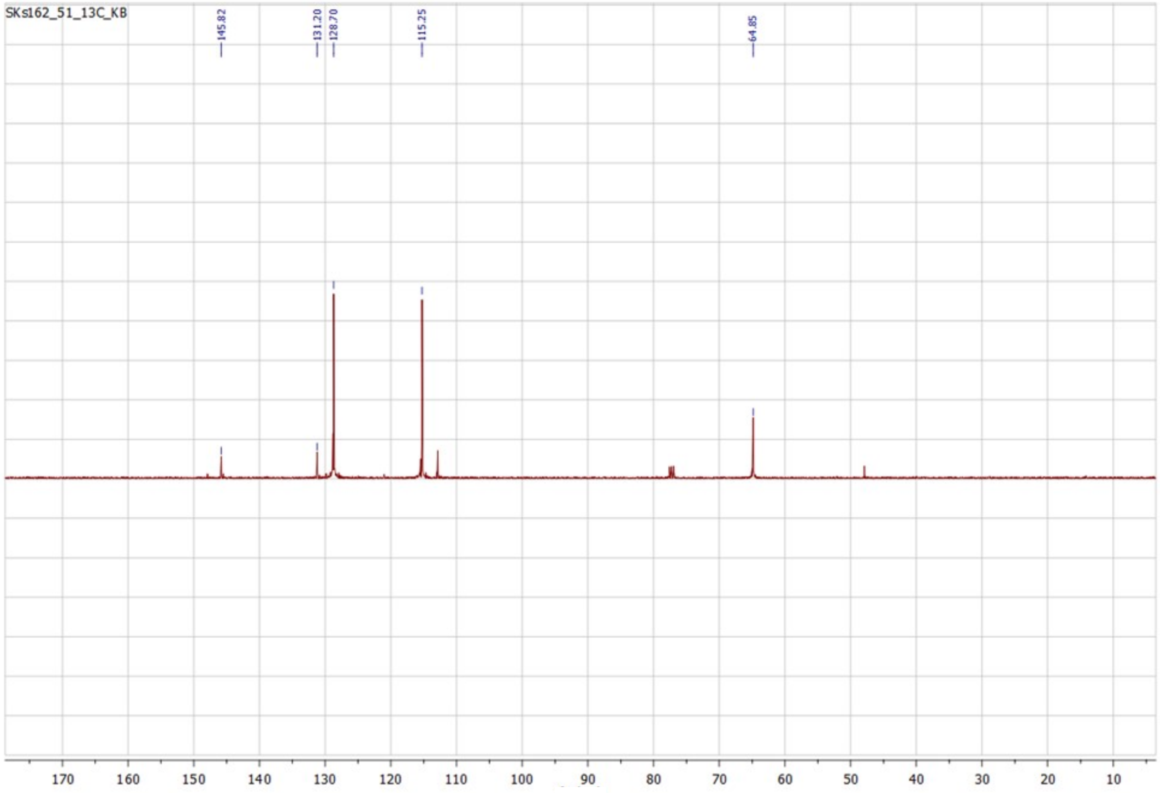


**Figure S6.** $^{13}$C NMR spectrum of **p-aminobenzyl alcohol (4).**

## References:

S1. G. D. Vo and J. F. Hartwig, *J. Am. Chem. Soc.* 2009, **131**, 11049.
S2. H. Yang, Yo. Li, M. Jiang, J. Wang, H. Fu, *Chemistry - A European Journal*, 2011, **17,** 5652.