Electronic Supplementary Information

Cyclodextrins as Effective Additives in AuNPs-Catalyzed Reduction of Nitrobenzene Derivatives in a Ball-Mill

Stéphane Menuel,[a] Bastien Léger, [a] Ahmed Addad,[b] Eric Monflier,[a] and Frédéric Hapiot*[a]

[a] Univ. Artois, CNRS, Centrale Lille, ENSCL, Univ. Lille, UMR 8181, Unité de Catalyse et de Chimie du Solide (UCCS), F-62300 Lens, France.
[b] UMET, UMR CNRS 8207, Université Lille 1, 59655 Villeneuve d'Ascq Cédex, France.

E-mail: frederic.hapiot@univ-artois.fr.

Materials and methods

All chemicals were used as received. Analytical thin-layer chromatography (TLC) was performed on aluminum-backed silica gel. Reactions were conducted using a laboratory-scale ball-mill (Retsch MM400) equipped with 10 mL zirconia grinding jars containing one zirconia ball (9 mm ⌀, 5.4 g). The grinding jars performed radial oscillations in a horizontal position. The frequency of the ball-mill represents the oscillation of the milling beakers (frequency of the rocking back-and-forth motion conducted by the reaction jar holder). It is not related to the number of impacts, which depends on the frequency of the ball-mill, the number of balls, and the filling degree. The data were collected as follows: The ball-mill was stopped at a given time. A sample of the powder was collected and analyzed. The ball-mill was then restarted. The procedure was repeated as often as necessary. Each reaction was repeated twice to ensure the repeatability of the results. Each data point is the average of the two obtained values. Samples were collected and analyzed by GC-MS – QP2010 SE with a 30m ZB-WAX column (carrier gas He, column flow 2.90 mL/min, 80 °C to 230 °C at 5 °C/min) to determine the conversion and selectivity. NMR spectra were recorded on a spectrometer operating at 300 MHz for ^{1}H nuclei and 75 MHz for ^{13}C nuclei in D_2O (99.92% isotopic purity). Mass spectra were recorded on a MALDI-TOF−TOF spectrometer in positive reflectron or linear mode with 2,5-dihydroxybenzoic acid (2,5-DHB) as matrix. Transmission electron microscopy (TEM) images were recorded on a TECNAI electron microscope operating at an accelerating voltage of 200 kV. The powder was deposited on a carbon coated copper grid. Metal particle size distributions have been determined from the measurement of ca. 225 particles found in arbitrarily chosen area of the images using the SCION Image software. X-ray photoelectron spectroscopy (XPS) experiments were performed using an AXIS Ultra DLD Kratos spectrometer equipped with a monochromatized aluminum source (Al Kα =1486.7 eV) and charge compensation gun. All binding energies were referenced to the C 1s core level at 285 eV.

Figure S1. TEM images obtained after reduction of $AuCl_3$ (0.016 mmol) by $NaBH_4$ (1.64 mmol) without any stabilizer.

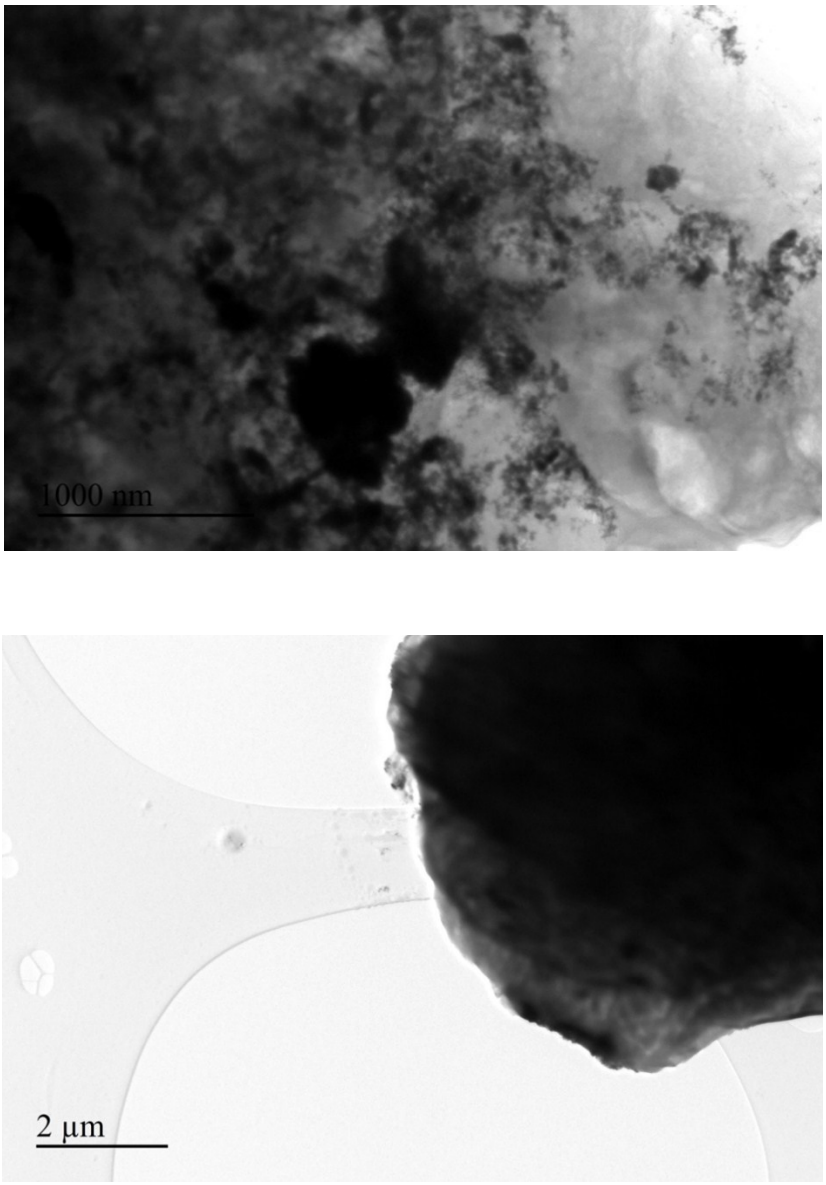


Figure S2. Partial MALDI-TOF/TOF MS spectrum of native β-CD ($C_{42}H_{70}O_{35}$) ball-milled for 5 min at 30 Hz in the presence of 5 wt% $AuCl_3$.

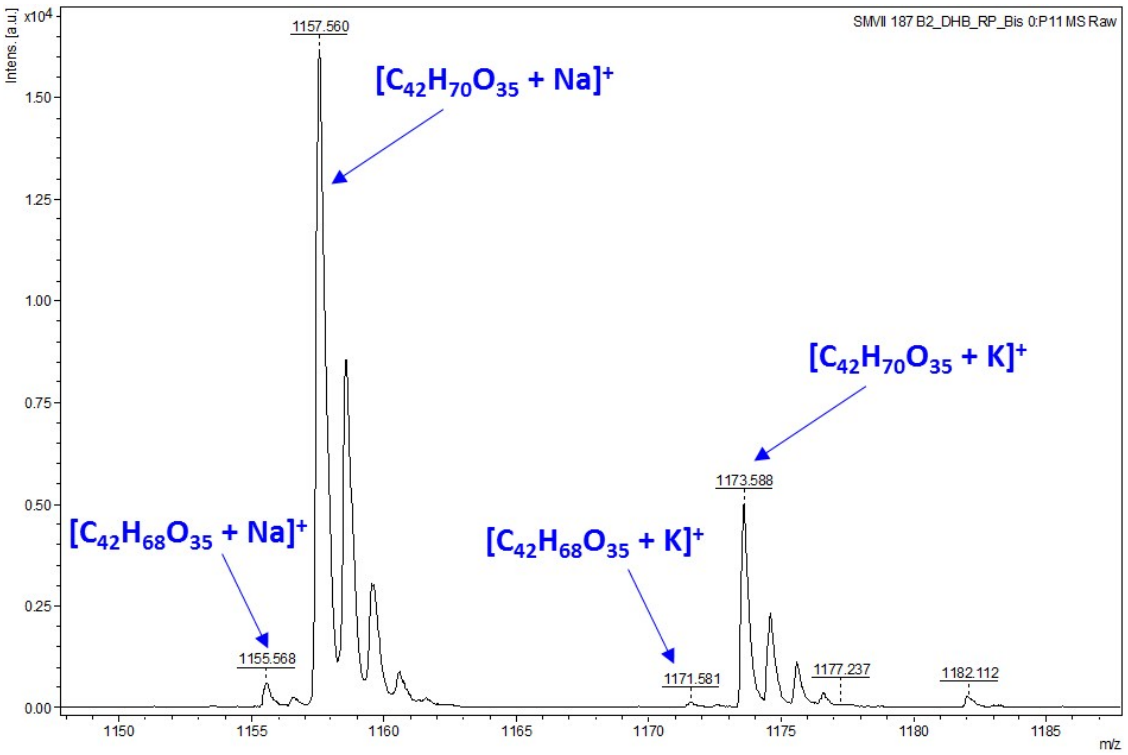


Figure S3. MALDI-TOF/TOF MS spectrum revealing the fragmentation pattern of AuNPs synthesized by ball-milling the native β-CD and 5 wt% $AuCl_3$ for 5 min at 30 Hz.

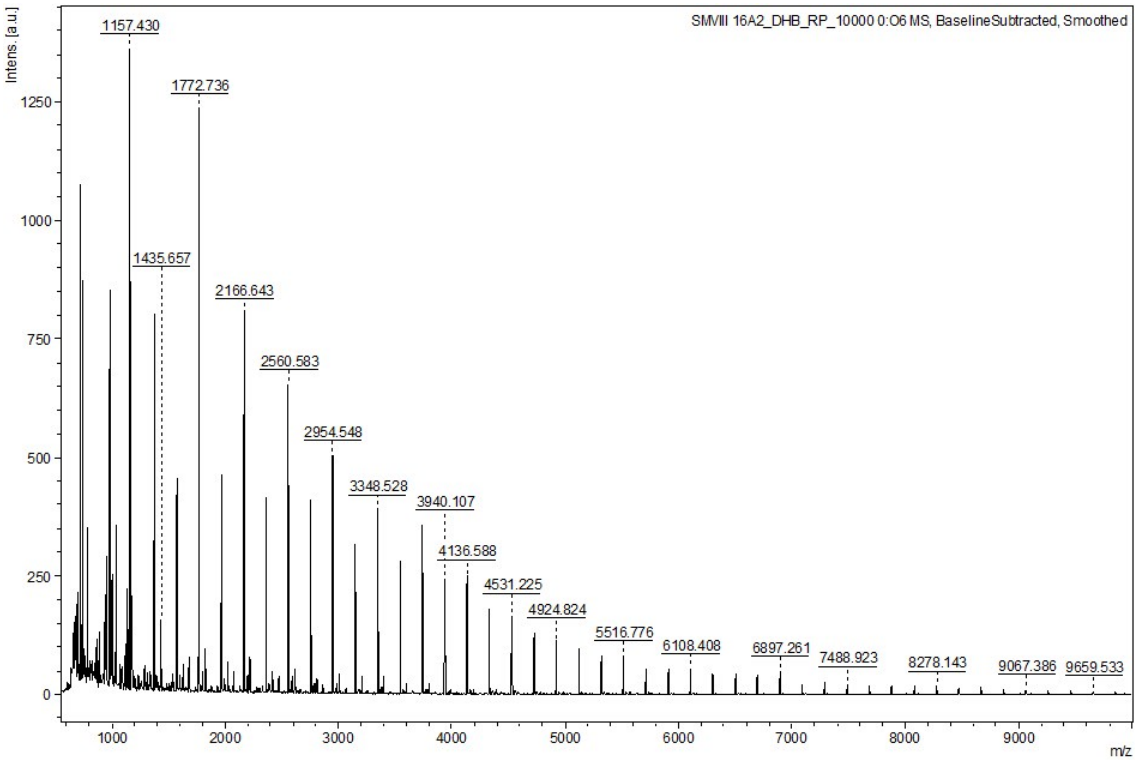
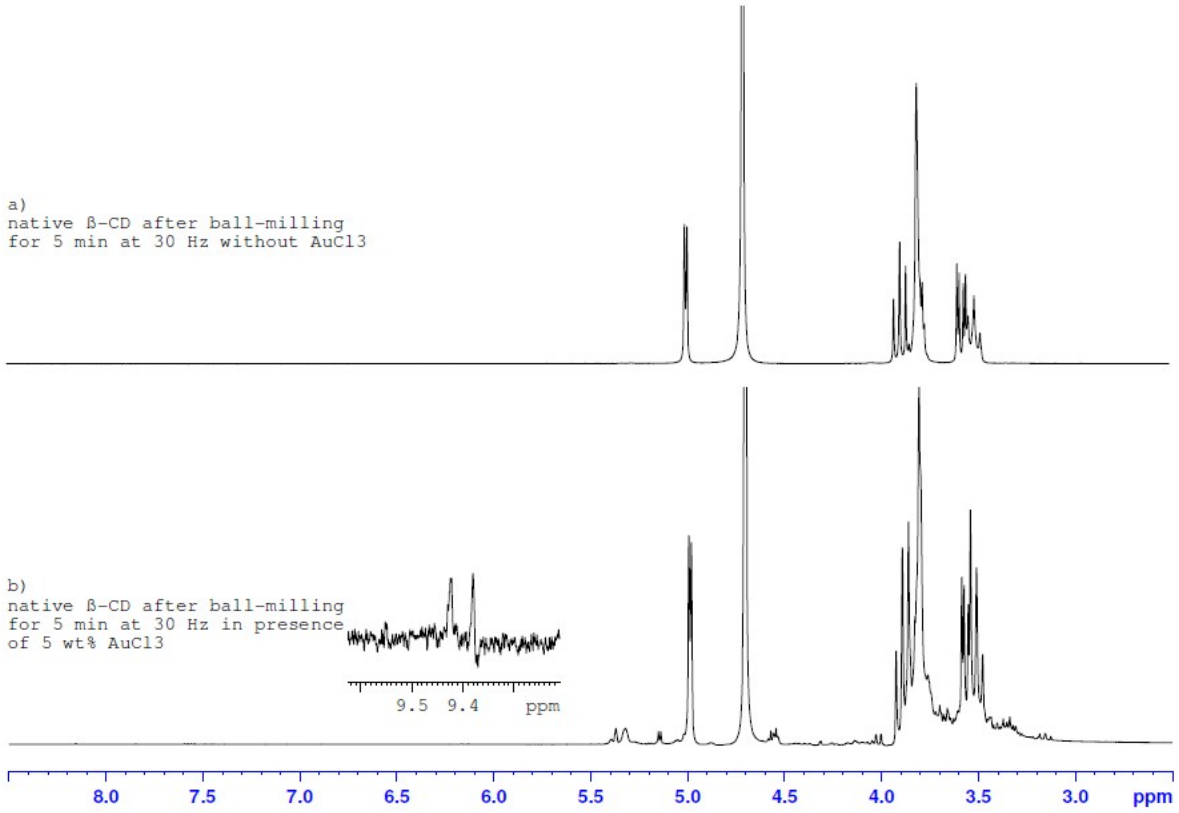


Figure S4. ^{1}H NMR spectra of native β-CD ball-milled for 5 min at 30 Hz in the absence of $AuCl_3$ (top) and in the presence of 5 wt% $AuCl_3$ (down).



The presence of two signals in the 10-9 ppm region is indicative of formyl protons resulting from oxidation of the hydroxyl groups located on both the primary and secondary faces of the native β-CD.

Figure S5. XPS spectrum for the Au 4f signal of a sample resulting from ball-milling a mixture of 2-chloroaniline (0.823 mmol), $NaBH_4$ (1.64 mmol), and saccharide-stabilized AuNPs (0.016 mmol) at 30 Hz for 15 min.

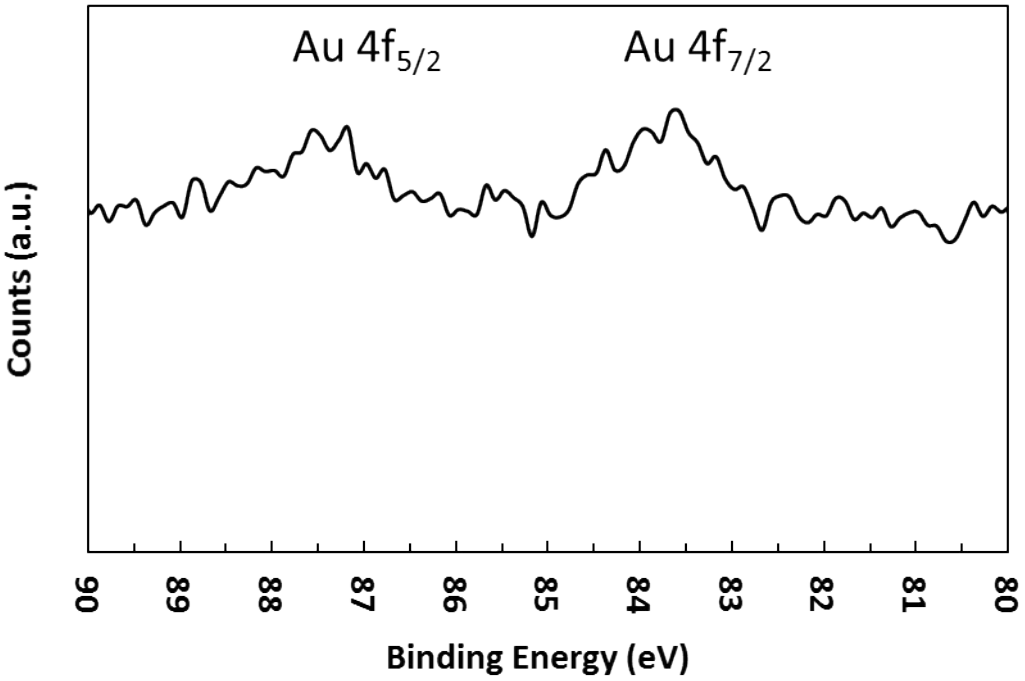
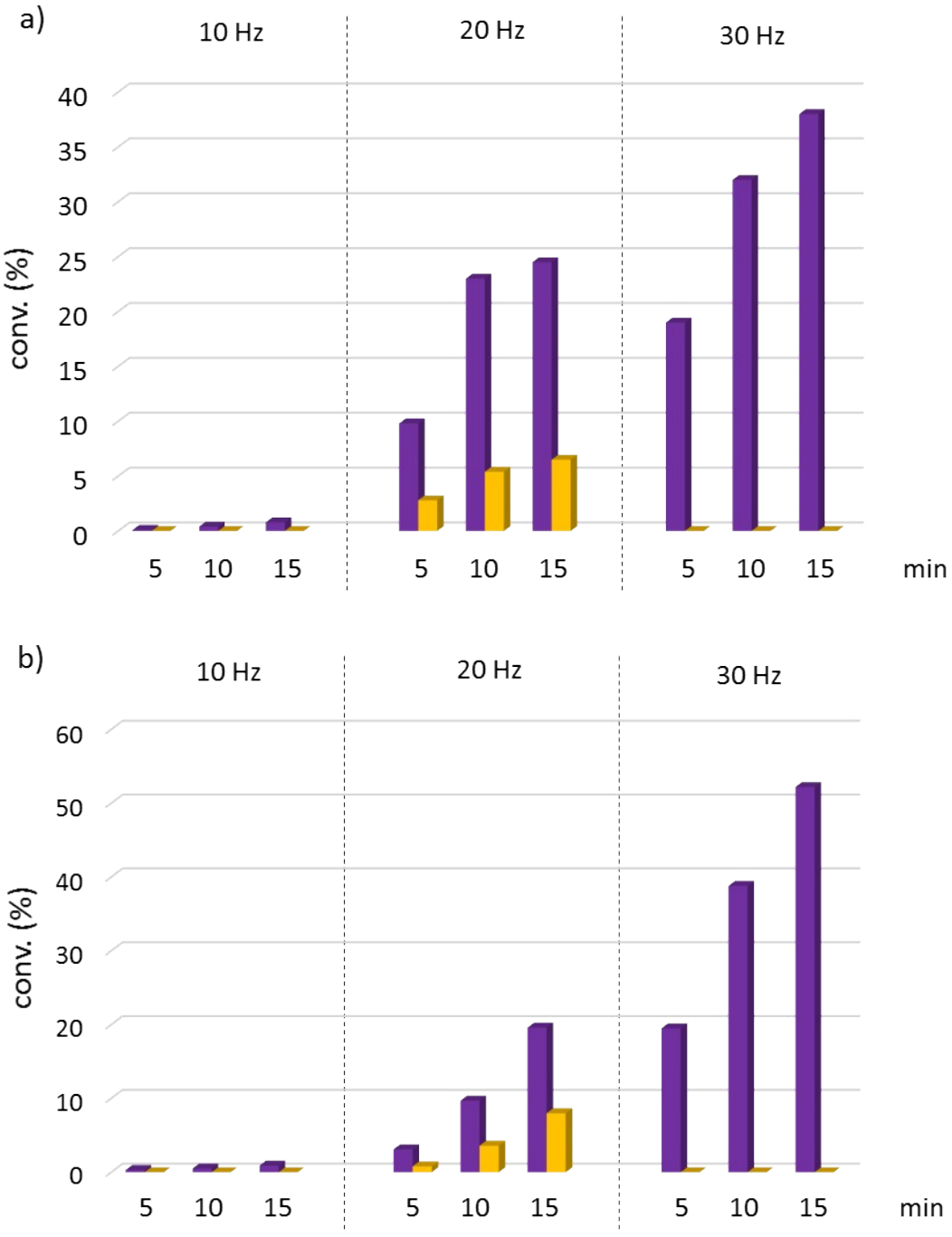


Figure S6. Variation of the ball-milling frequency in the AuNPs-catalyzed reduction of 1-chloro-2-nitrobenzene in the presence of a) native α-CD, b) native γ-CD and c) potato starch. Violet bars: 2-chloroaniline; orange bars: 2-chlorophenylhydroxylamine.



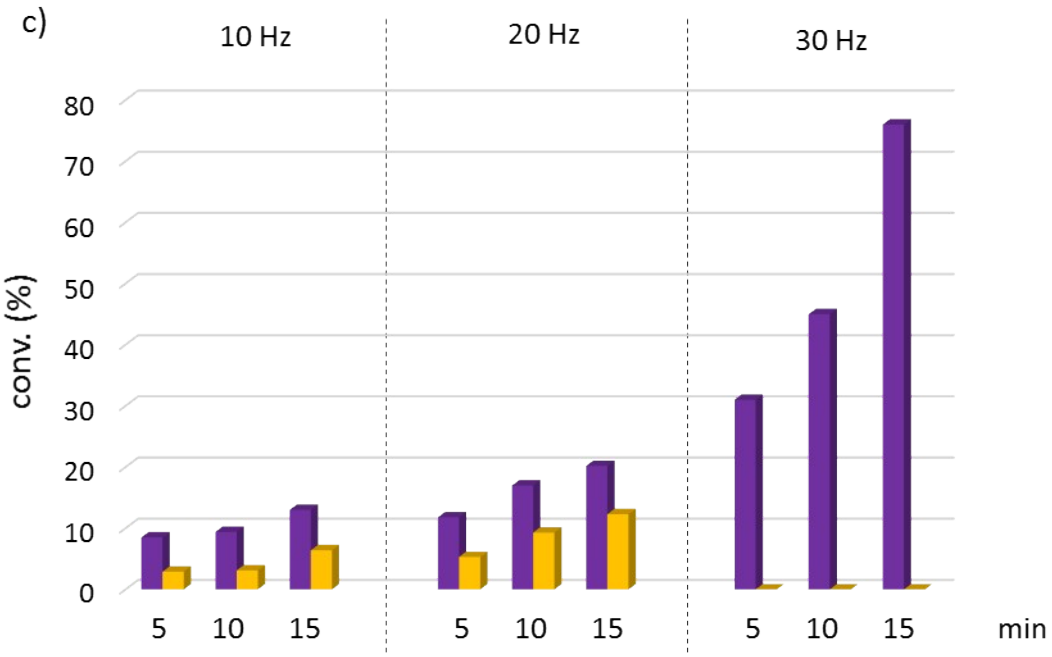
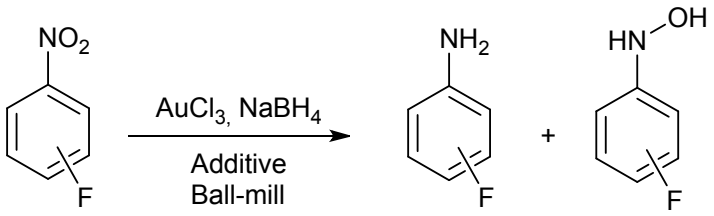

c)
10 Hz
20 Hz
30 Hz
conv. (%)
80
70
60
50
40
30
20
10
0
5
10
15
5
10
15
5
10
15
min

Table S1. AuNP-catalyzed reduction of fluoronitrobenzene derivatives using a ball-mill.



Time (min)	fluoronitrobenzene	Mp (°C)	Conv. (%)	aniline derivative (%)	*N*-phenyl Hydroxylamine (%)
15	*para*-isomer	21	100	100	0
114	*para*-isomer	21	100	100	0
15	*meta*-isomer	1.7	100	38.1	61.9
114	*meta*-isomer	1.7	100	100	0
15	*ortho*-isomer	-9/-6	100	34.5	65.5
114	*ortho*-isomer	-9/-6	100	100	0

Conditions: AuNP prepared by ball-milling CD (0.881 mmol) and 5 mg of $AuCl_3$ (0.016 mmol) at 30 Hz for 5 min. Subsequent addition of substrate (0.823 mmol) and $NaBH_4$ (1.64 mmol). Ball-milling frequency = 30 Hz.