Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Single molecule study of samarium oxide nanoparticles as a purely heterogeneous catalyst for one-pot aldehyde chemistry

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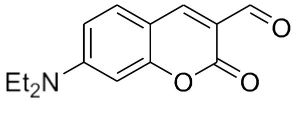
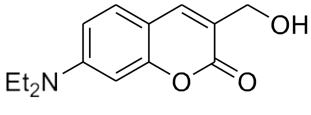
*Synthesis of **2***



2

Compound **2** was prepared according to literature procedures.[S1] EI-MS: 245.1 $[M]^{+}$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.1 (1H, s), 8.2 (1H, s), 7.4 (1H, d, 7 Hz), 6.6 (1H, d, 8 Hz), 6.5 (1H, s), 3.4 (4H, q, 5 Hz), 1.2 (6H, t, 5 Hz). ^{13}C NMR ($CDCl_3$): δ 187.9, 35 161.8, 158.9, 145.3, 132.5, 114.5, 110.4, 108.4, 97.4, 45.4, 12.4.

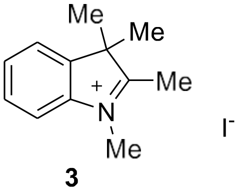
*Synthesis of **1***



1

A solution of **2** (170 mg, 0.7 mmol) and $NaBH_4$ (25 mg, 0.7 mmol) in MeOH (25 mL) was stirred at 0 °C for 20 min and later at room temperature for 3h. The reaction was quenched with H_2O (25 mL) and the solution was extracted with $CHCl_3$ (3 × 15 mL). The organic phase was combined, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The mixture was purified by column chromatography [SiO_2/CH_2Cl_2-EtOAc 2:1 (v/v)] to yield the product (124 mg, 72%) as a yellow powder. EI-MS: 247.3 $[M]^{+}$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5 (1H, s), 7.2 (1H, d, 9 Hz), 6.6 (1H, d, 8 Hz), 6.4 (1H, s), 4.5 (2H, s) 3.4 (4H, q, 5 Hz), 1.2 (6H, t, 5 Hz). ^{13}C NMR ($CDCl_3$): δ 162.8, 156, 150.5, 140, 128.8, 120.2, 109, 108.2, 97.2, 61.5, 44.7, 12.4.

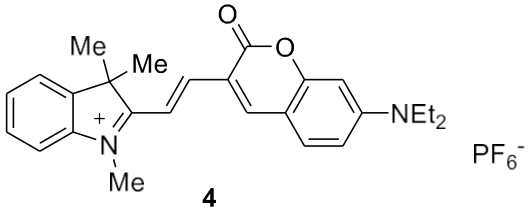
*Synthesis of the iodide salt of **3***



3

Compound **3** was prepared according to literature procedures.[S2] EI-MS: 174.1 $[M]^{+}$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5-7.63 (4H, m), 4.3 (3H, s), 3.1 (3H, s), 1.7 (6H, s). ^{13}C NMR ($CDCl_3$): δ 196.5, 148, 140.5, 127.9, 125.6, 119.8, 110.5, 42.8, 31.6, 27.2, 9.1.

Synthesis of the hexafluorophosphate salt of ***4***



4

Compound **4** was prepared according to literature procedures.[S3] ESI-MS: 401.3 $[M]^+$. ^{1}H NMR (300 MHz, CD_3CN): δ 8.4 (1H, s), 8.1 (1H, d, 16 Hz), 7.9 (1H, d, 16 Hz), 7.7-7.5 (4H, m), 6.8 (1H, dd, 2 and 9 Hz), 6.5 (1H, d, 2 Hz), 3.9 (3H, s), 3.5 (4H, q, 7 Hz), 1.8 (6H, s), 1.2 96H, t, 7 Hz). ^{13}C NMR (CD_3CN): δ 180.9, 161.4, 158.7, 154.3, 150.7, 143, 141.5, 135, 128.9, 128.6, 122.4, 115.1, 114.5, 110.8, 108.7, 97.2, 52.5, 46, 35.8, 28.2, 12.8.

References

(S1) Wu, J. *et al.* Fluorescence turn on of coumarin derivatives by metal cations: a new signaling mechanism based on C=N isomerization. *Org. Lett.* **9,** 33-36 (2007).
(S2) Tomasulo, M., Sortino, S., Raymo, F. M. Bichromophoric photochromes based on the opening and closing of a single oxazine ring. *J. Org. Chem.* **73,** 118-126 (2008).
(S3) Deniz, E., Sortino, S., Raymo, F. M. Fluorescence switching with a photochromic auxochrome. *J. Phys. Chem. Lett.* **1,** 3506-3509 (2010).

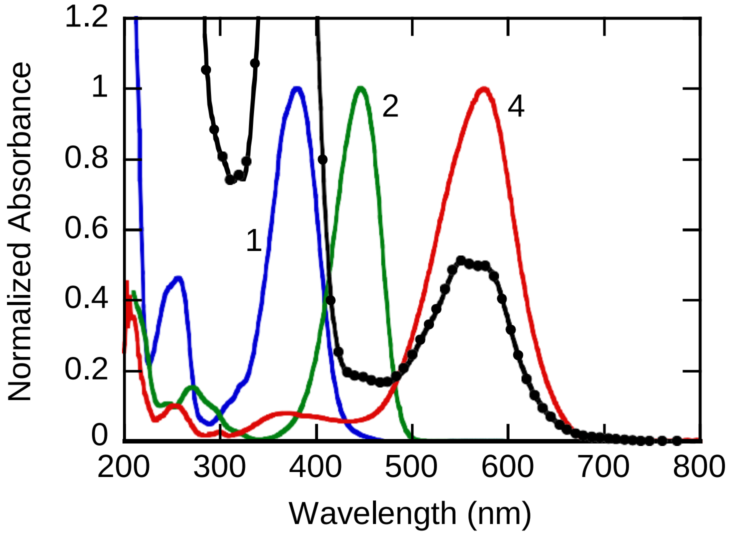


Figure S1. Normalized absorption spectra for compounds **1**, **2** and **4**. The black dotted trace depicts a typical absorption spectrum for reactions **a**-**d**.

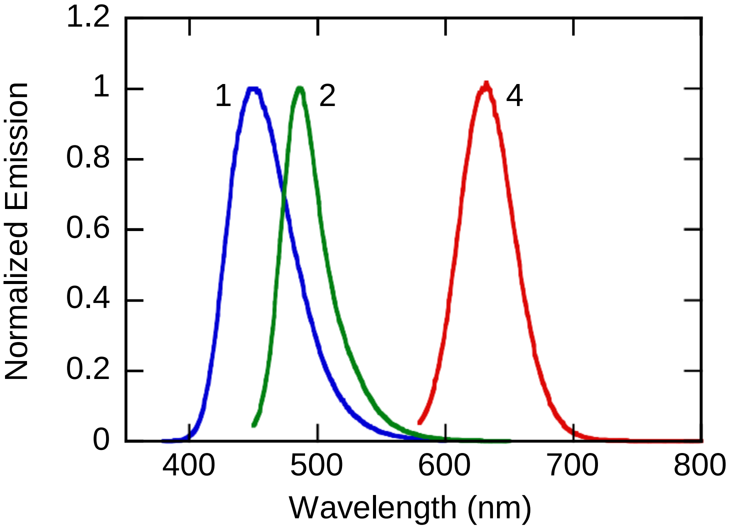


Figure S2. Normalized emission spectra for compounds **1** (λ_{Ex} = 370 nm), **2** (λ_{Ex} = 440 nm) and **4** (λ_{Ex} = 570 nm).

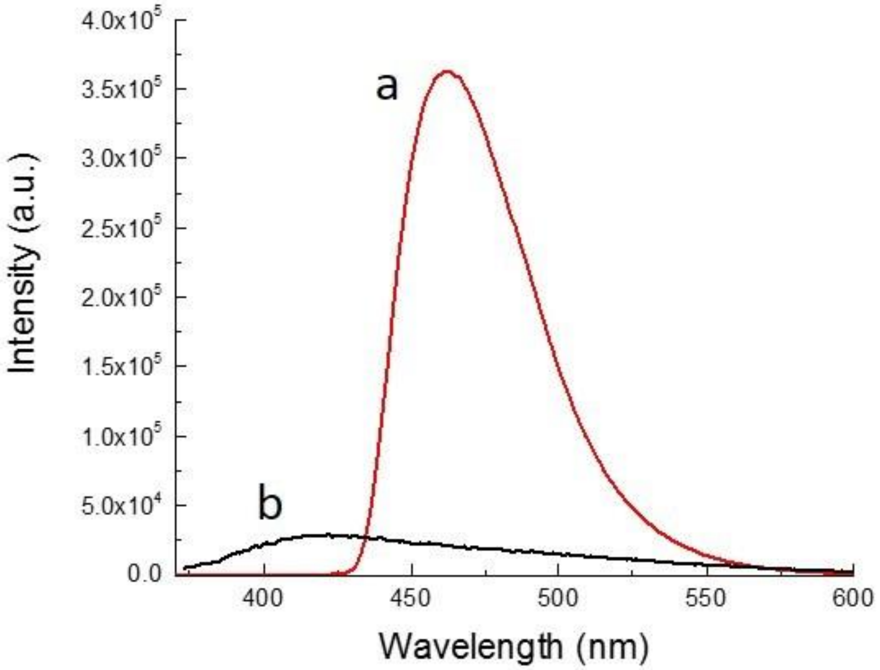


Figure S3. Emission spectrum of (**a**) supernatant obtained by centrifuging (3000 rpm, 30 min) a solution of Sm_2O_3NP and **1** in EtOH previously stirred at 65°C for 24 h and (**b**) unreacted polydisperse Sm_2O_3NP dissolved in DMSO. Note the emission of the activated alcohol species centred at 465 nm lies between the emission wavelengths of **1** (450 nm) and **2** (490 nm). λ_{Ex} = 350 nm.

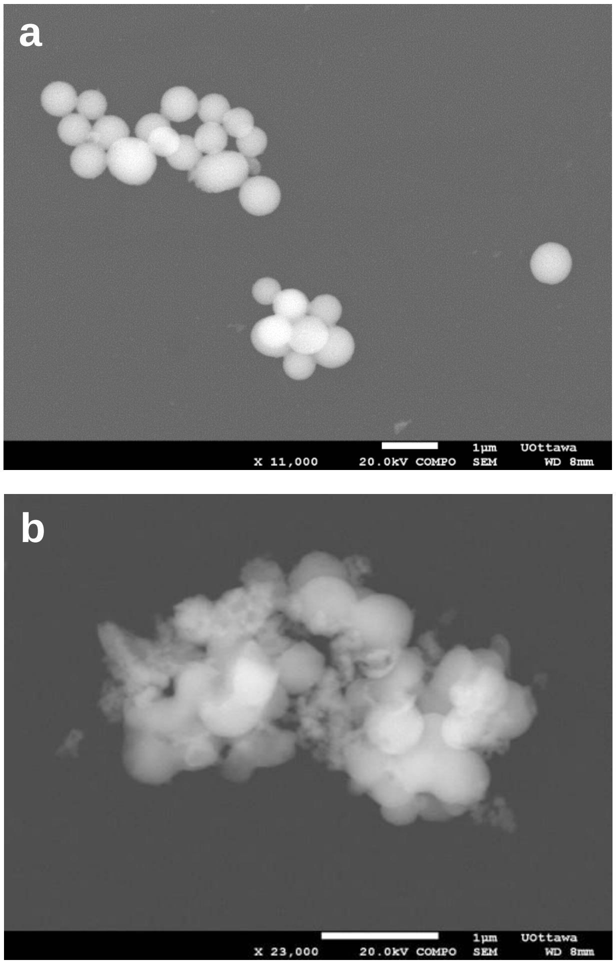


Figure S4. SEM image of Sm_2O_3NP before (**a**) and after (**b**) reaction **d**.

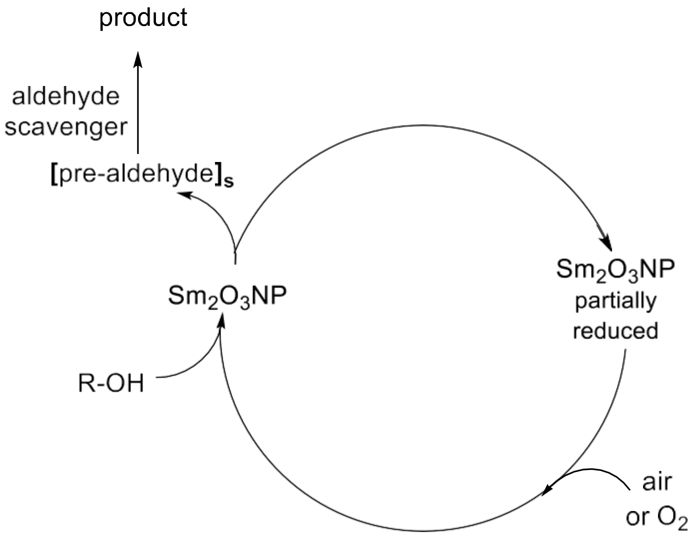


Figure S5. Proposed scheme for one-pot Sm_2O_3NP-catalysed aldehyde chemistry and subsequent regeneration of the catalyst surface.

Single Molecule Fluorescence Microscopy (Video description):

Single molecule experiments were conducted by recording TIRFM image sequences while flowing an equimolar mixture (1–5 nM) of **1** and **3** in EtOH atop a glass microscope coverslip spin-coated with Sm_2O_3NP. These videos were recorded at a rate of 10 frames/s with an integration time of 100 ms, and ranged in length from 1000 to 2000 frames. The representative image sequence entitled Supplementary Video 1 is comprised of the first 250 frames of a 2000 frame video (to facilitate greater file compression) prior to background subtraction and shows bright fluorescence bursting events against a dark background in an 80×80 μm^2 area at 10 frames/s. This type of videos should be viewed under dim light to appreciate well the bursting events and the repetitive locations at which they occur.

These fluorescence bursting events represent the formation of single molecules of the fluorescent product **4** as a direct result of catalysis by Sm_2O_3NP. Repeated formation of single fluorescent molecules, and thus repeated bursting events, at individual locations indicate heterogeneous catalysis. The fluorescence intensity at various 3×3 pixel locations in such TIRFM image sequences can be plotted as a function of time in order to generate unique intensity-time trajectories for each location (e.g. Figure 2 in the main text).

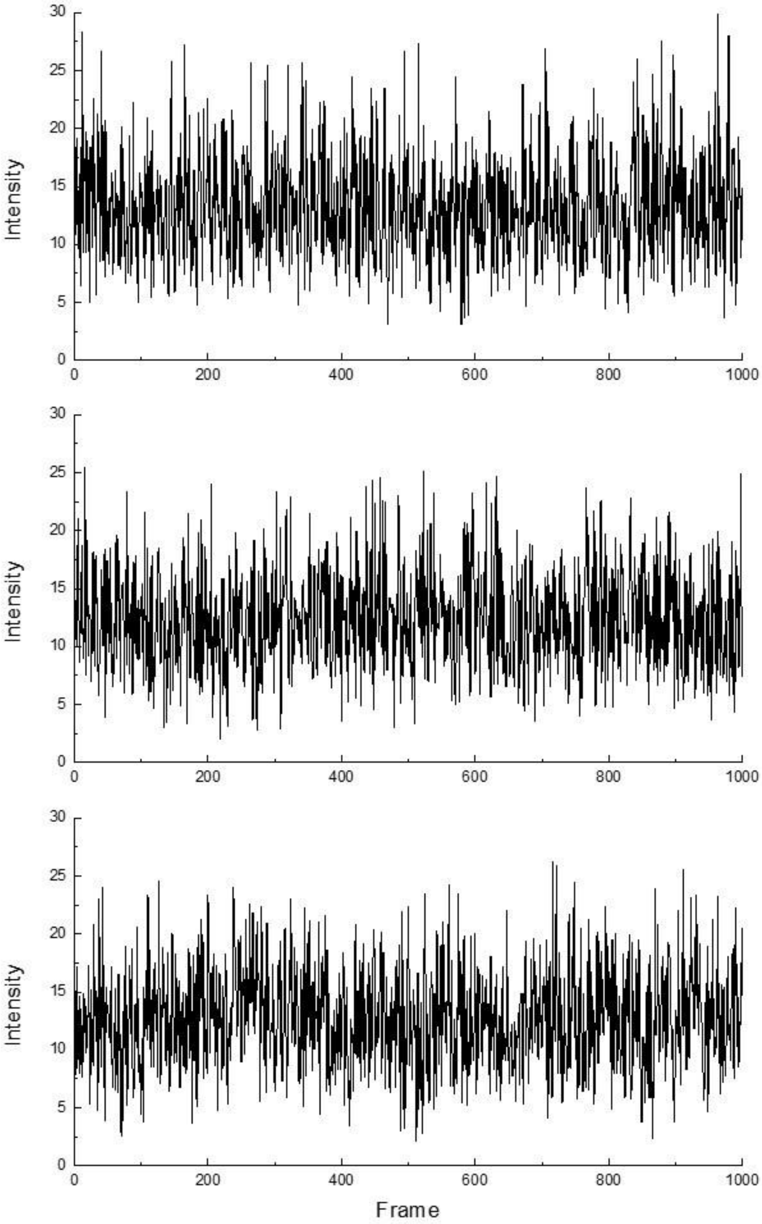


Figure S6. Representative intensity-time trajectories showing baseline background scattering, extracted from 3×3 pixel regions of interest in a 100 s TIRFM image sequence recorded at room temperature while flowing an equimolar solution of **1** and **3** atop a microscope coverslip spin-coated with Sm_2O_3NP. Exposure time was 100 ms per frame.

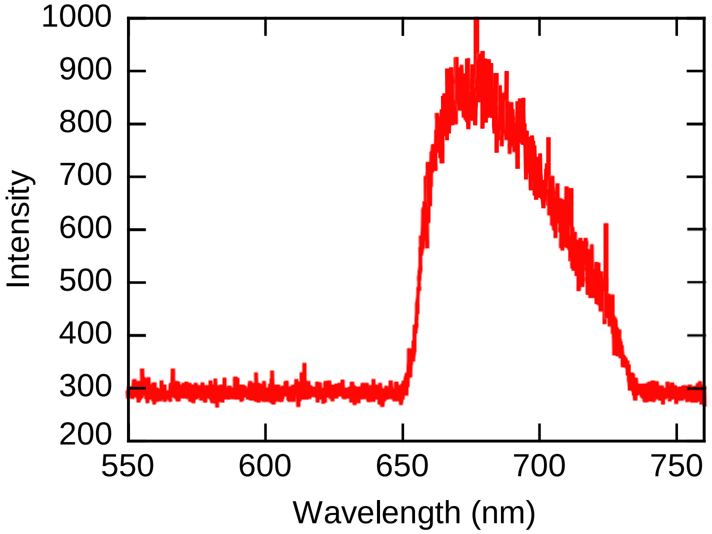


Figure S7. Spectral information of the detected bursting events measured by passing the epifluorescent signal through a spectrograph (λ_{Ex} = 637 nm) and using a 690/70 nm band pass emission filter installed into the Fluorescent Lifetime Imaging system.

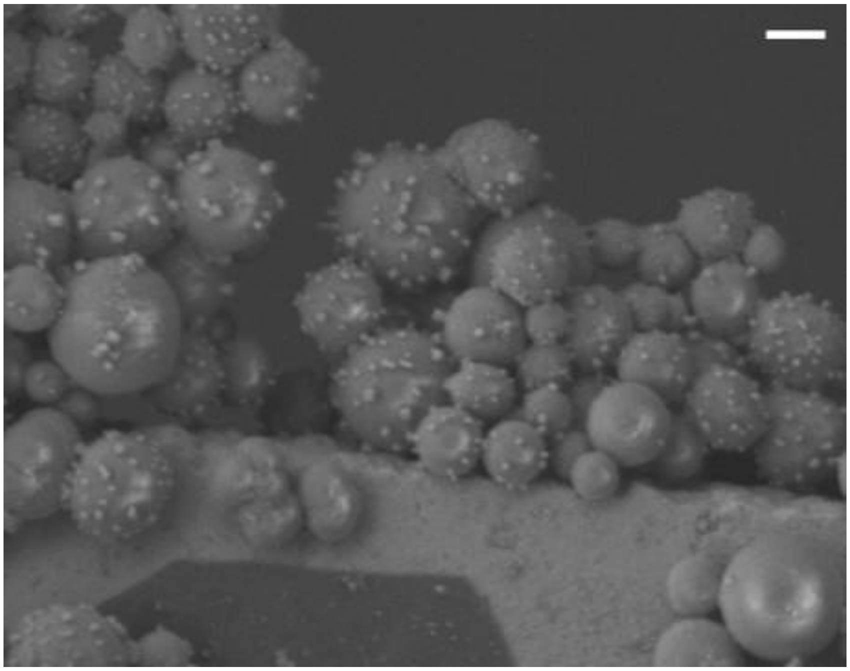


Figure S8. Representative SEM image demonstrating that small catalytic Sm_2O_3NP are already present in the original polydisperse nanomaterial. Scale bar is 1 µm.

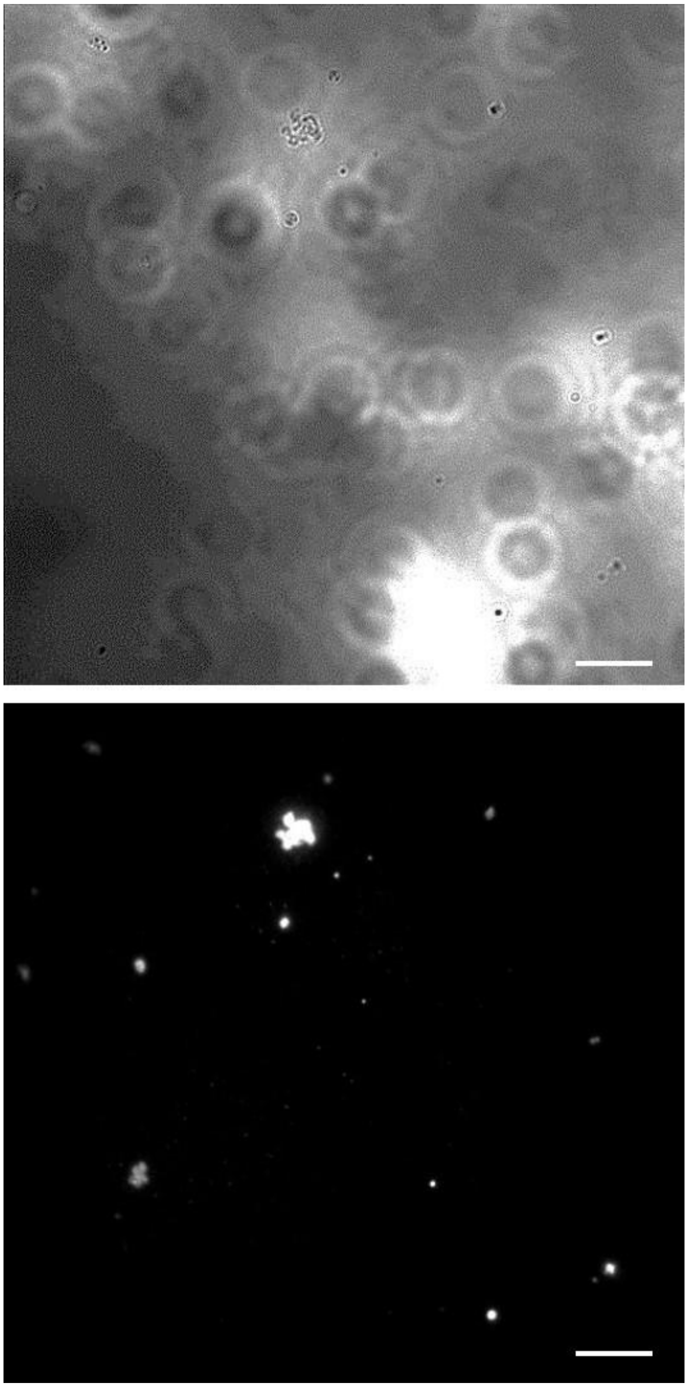


Figure S9. Widefield transmission (**a**) and TIRFM (**b**) images of Sm_2O_3NP spin-coated onto a microscope coverslip. Scale bars are 10 µm.

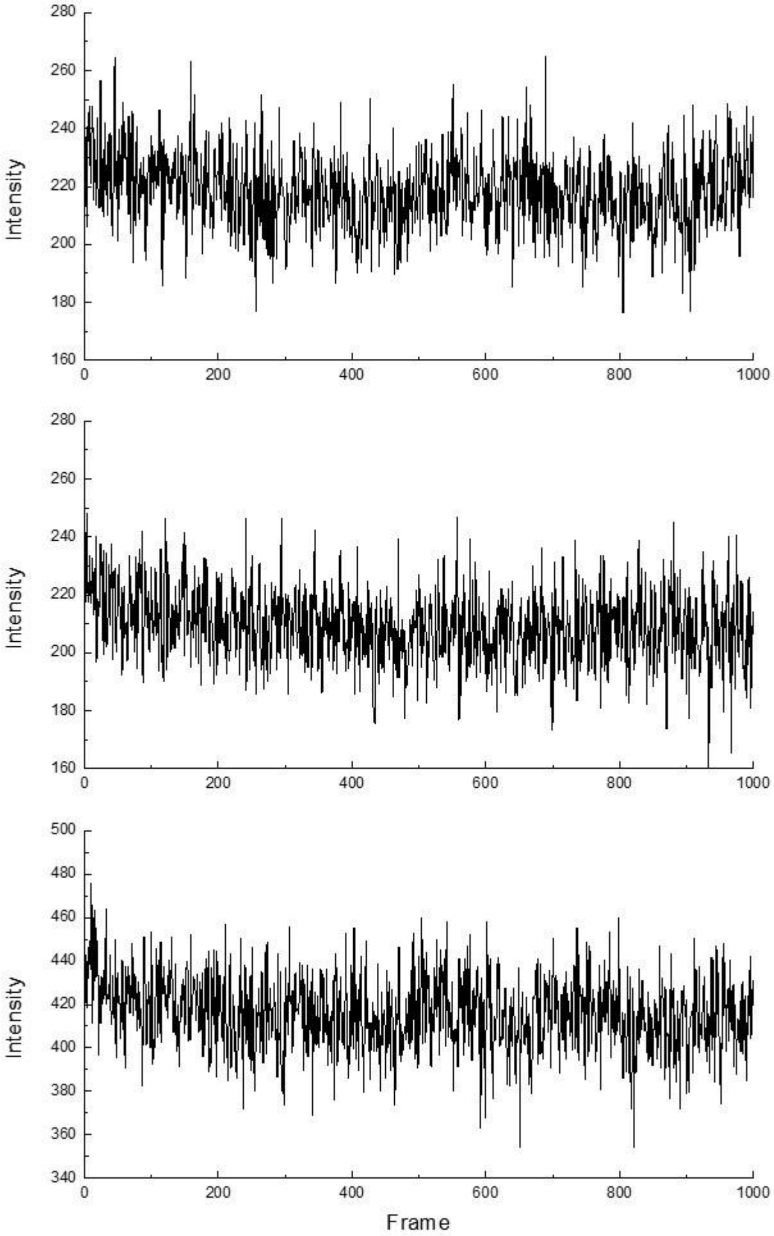


Figure S10. Representative intensity-time trajectories extracted from 3×3 pixel regions of interest located directly atop or adjacent to large Sm_2O_3NP visible in a TIRFM image sequence recorded while flowing only EtOH atop of a glass coverslip spin-coated with the catalyst. Exposure time was 100 ms per frame.

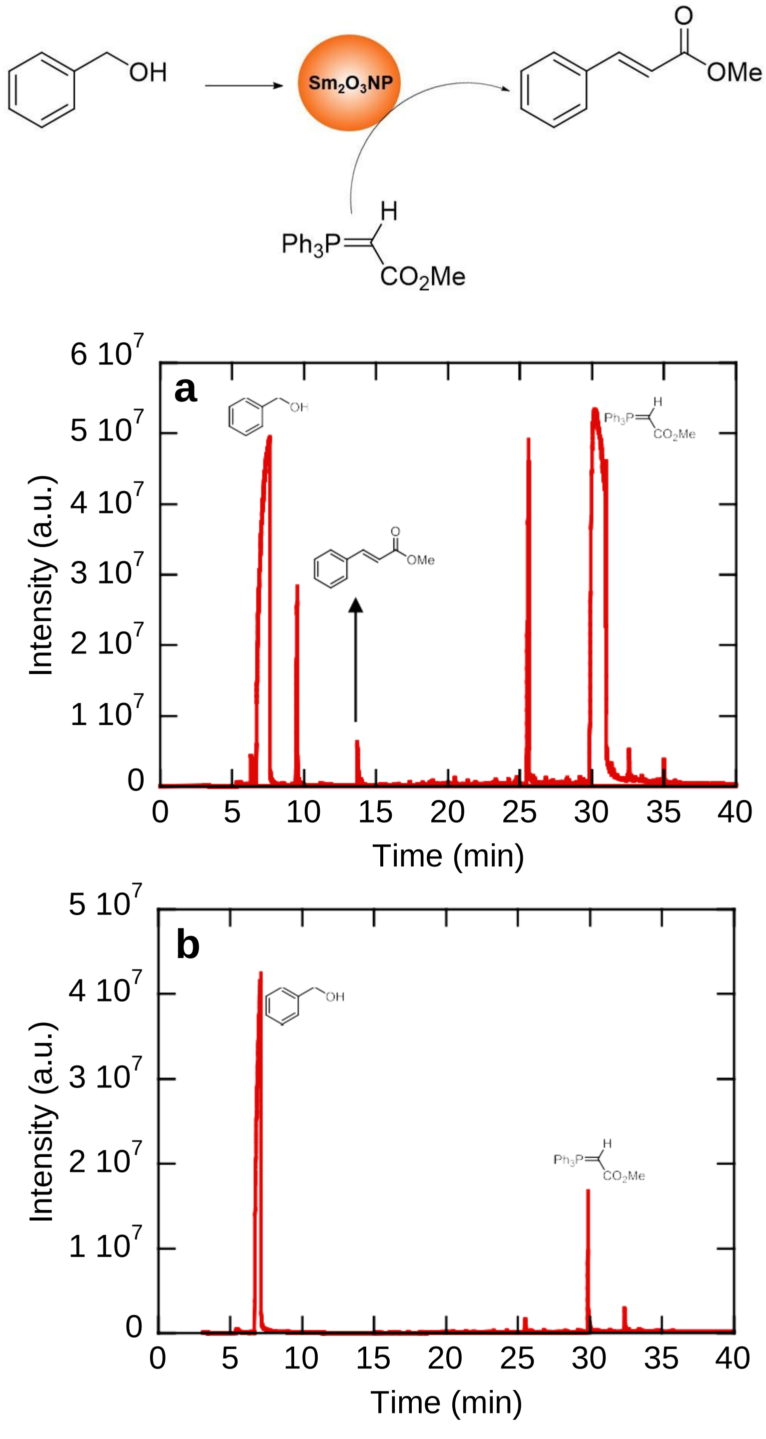


Figure S11. Top: proposed mechanism for the Sm_2O_3NP catalyzed alcohol oxidation and Wittig olefination as coupled processes. Bottom: gas chromatograms for the reaction between benzyl alcohol (7 min) and Sm_2O_3NP (**a**) in the presence and (**b**) in the absence of the Wittig reagent methyl(triphenylphosphoranylidene)acetate (32 min).