

Electronic Supplementary Information

Synergistic effect of nanoporous AuPd alloy catalysts on highly chemoselective 1,4-hydrosilylation of conjugated cyclic enones

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General Information

Scanning electron microscope (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. TEM characterization was performed using a JEM-2100F TEM (JEOL, 200 kV) equipped with double spherical aberration (Cs) correctors for both the probe-forming and image-forming lenses. The XPS measurements were carried out using a VG ESCALAB 250 spectrometer (Thermo Fisher Scientific K.K.) employing monochromatic Al K X-ray radiation. The base pressure of the analysis chamber was less than 10^{-8} Pa. ¹H NMR and ¹³C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) spectrometers. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl₃ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broadened), and coupling constants (Hz). ¹³C NMR spectra were recorded on JEOL JNM AL 400 (100.5 MHz) spectrometers with complete proton decoupling, and chemical shift reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer and JEOL JMS-700 MStation operator. Column chromatography was carried out employing silica gel 60 N (neutral, 40~63 μ m, Merck KGaA Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials. Au (99.99%) and Pd (99.99%) are purchased from Tanaka Kikinzoku Hanbai K.K. and Al (99.99%) is purchased from Mitsuwa's Pure Chemicals, respectively. PdNPore-2 and PdNPore-3 were prepared following our reported methods.¹ AuPdNPs was prepared following the reported literature.² HSiEt₃ and conjugated cyclic enones are commercially available, which are used as received. 5-Methyl-2-cyclohexene-1-one was synthesized according to the literature.³ Structures of the known products **2a**,⁴ **2b**,⁴ **2f**⁵ were identified by ¹H, ¹³C NMR and HRMS comparing with the reported authentic compounds. The new products were confirmed by ¹H, ¹³C NMR and HRMS.

References:

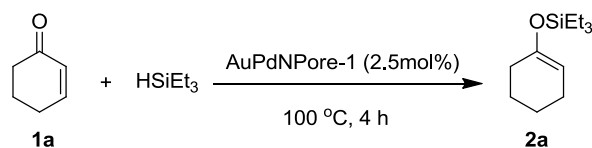
1. (a) S. Tanaka, T. Kaneko, N. Asao, Y. Yamamoto, M.-W. Chen, W. Zhang, A. Inoue, *Chem. Commun.*, 2011, **47**, 5985; (b) T. Kaneko, S. Tanaka, N. Asao, Y. Yamamoto, M.-W. Chen, W. Zhang, A. Inoue, *Adv.*

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2. J. A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G. L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R. L. Jenkins, A. F. Carley, D. Knight, C. J. Kiely, G. J. Hutchings, *Nat. Chem.*, 2011, **3**, 551
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Fabrication of the nanoporous AuPd (AuPdNPore) alloy catalysts. Au (99.99%), Pd (99.99%) and Al (99.99%) were melted with electric arc-melting furnace under an Argon atmosphere to form AuPdAl alloy. A single roller melt-spinning apparatus was used to prepare the ribbon of AuPdAl alloys with 20-50 μm in thickness and 2-5 mm in width. The resulting alloys were treated with 20 wt. % NaOH solution for 36 h at room temperature to give the AuPdNPore catalysts. The resulting material was washed with pure water and acetone followed by drying under reduced pressure, which was used as catalyst for 1,4-hydrosilylation.

Representative procedure of 1,4-hydrosilylation of conjugated cyclic enones using AuPdNPore-1 as a catalyst (Tables 1, entry 5).



To a mixture of **1a** (200 μl , 2 mmol) and HSiEt_3 (320 μl , 2.00 mmol) was added AuPdNPore-1 catalyst (2.5 mol%, 7.5 mg) at room temperature. The reaction mixture was stirred at $100\text{ }^\circ\text{C}$ for 4 h and monitored by TLC. After reaction, the AuPdNPore-1 catalyst was recovered by filtration and washed with diethyl ether. The recovered AuPdNPore catalyst was washed with acetone, diethyl ether, and acetone, subsequently. The catalyst was dried under vacuum for reuse. After concentration, the residue was purified with a Merck silica gel chromatography which was pretreated with a mixture of hexane and Et_3N (100:1) to afford **2a** (365 mg, 86%).

High resolution TEM (HRTEM) of AuPdNPore-2 and AuPdNPore-3

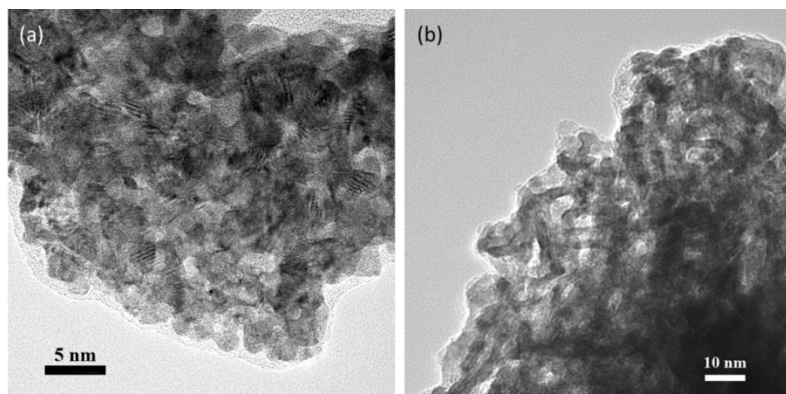


Fig S1. HRTEM images of AuPdNPore-2 (a) and AuPdNPore-3 (b).

STEM-EDS mapping of AuPdNPore-1

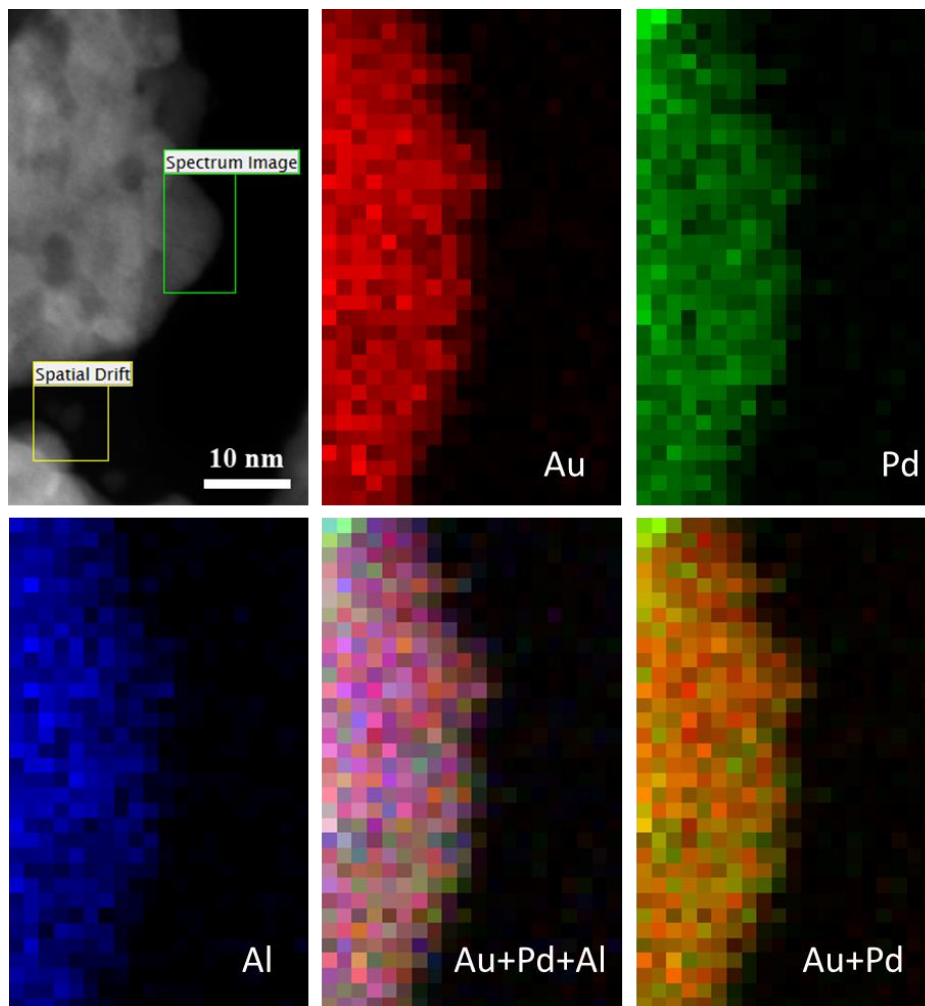


Fig S2. STEM-EDS mapping of as-prepared AuPdNPore-1.

XPS of AuPdNPore (Au-XPS)

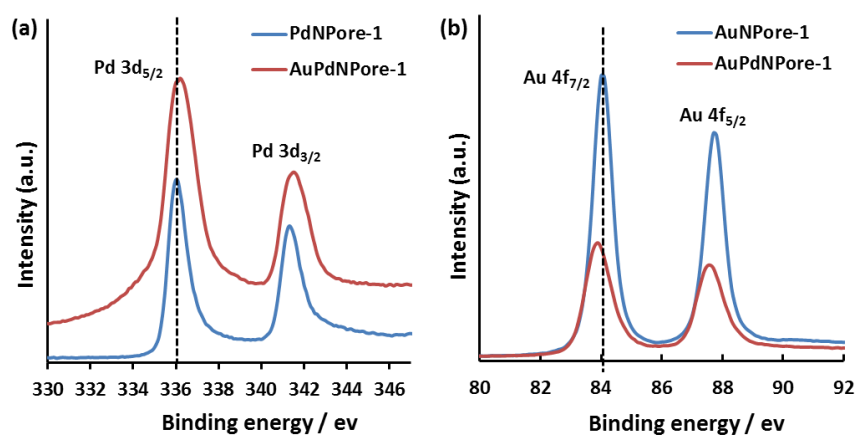


Fig S3. XPS characterization of AuPdNPore-1 vs PdNPore-1 (a) and AuPdNPore-1 vs AuNPore-1 (b).

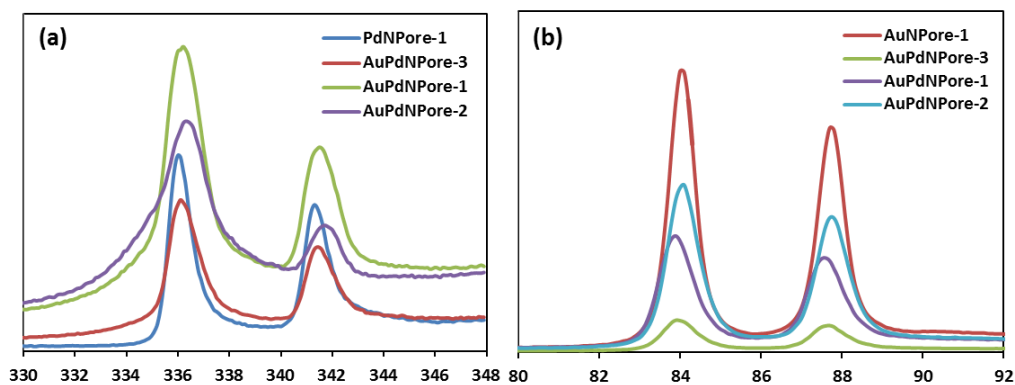


Fig S4. XPS characterization of AuPdNPore vs PdNPore (a) and vs AuNPore (b).

SEM images of fresh AuPdNPore-1 and after first cycle

After the first reuse, the AuPdNPore-1 catalyst did not show obvious changes in the nanopore and ligament sizes, and surface morphology.

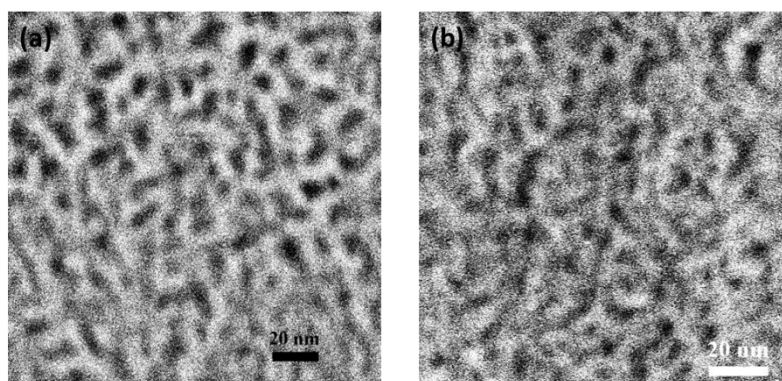
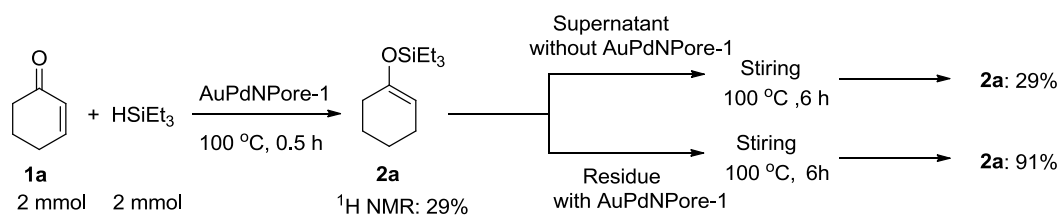


Fig S5. SEM images of AuPdNPore-1 catalyst; (a) fresh, (b) after first cycle.

Leaching experiments of AuPdNPore-1

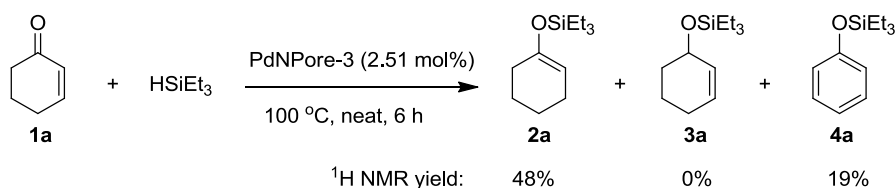


Scheme S1. Leaching experiments of AuPdNPore-1.

2-Cyclohexen-1-one **1a** was treated with HSiEt3 in the presence of AuPdNPore-1 catalyst (2.5 mol%) under neat condition at 100 °C. After 0.5 h, a part of supernatant was transferred to the other reaction vessel and **2a** was produced in 29 % $^1\text{H NMR}$ yield at this time. The supernatant was continuously heated at 100 °C in the absence of catalyst for 6 h, affording **2a** in 29 % $^1\text{H NMR}$ yield. In contrast, the residual containing the AuPdNPore-1 catalyst was completed in 6 h, giving **2a** in 91 % $^1\text{H NMR}$ yield.

Hydrosilylation of **1a** using PdNPore-3 (Pd₈₀Ni₁₃P₇) as catalyst

The PdNPore-2 catalyst was fabricated by electrochemical dealloying of Pd₃₀Ni₅₀P₂₀ metallic glass in 1 M H₂SO₄, which has been reported by our group including the fabrication method and characterization. The EDX analysis indicated that the composition of PdNPore-2 catalyst was Pd₇₈Ni₁₃P₉. Following this reviewer's comment, we further fabricated the nanoporous Pd₈₀Ni₁₃P₇ (PdNPore-3) catalyst under the same fabrication method by using Pd₂₀Ni₆₀P₂₀ metallic glass. The SEM image of PdNPore-3 was shown as Fig. S6. Under the standard reaction conditions, the hydrosilylation of **1a** using PdNPore-3 catalyst produced the corresponding 1,4-adduct **2a** and by-product **4a** in 48% and 19% yields, respectively, without forming the 1,2-adduct **3a** (Scheme S2).



Scheme S2. The catalytic activity of PdNPore-3 (Pd₈₀Ni₁₃P₇).

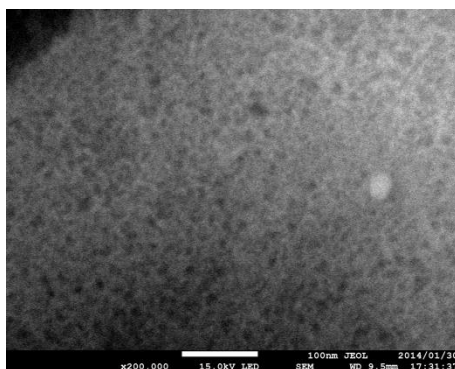


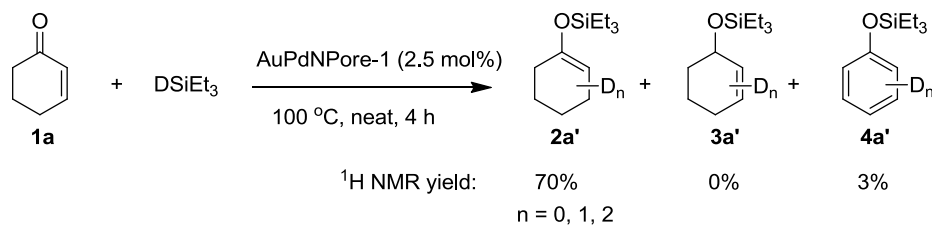
Fig S6. SEM image of PdNPore-3.

Hydrosilylation of **1a** with DSiEt₃ using AuPdNPore-1 as catalyst

We performed the AuPdNPore-1-catalyzed hydrosilylation of **1a** with DSiEt₃ instead of using HSiEt₃ under the standard conditions. The reaction showed a high 1,4-addition selectivity within 4 h at 100 °C, but the yield of the corresponding 1,4-adduct (70%) was lower than that using HSiEt₃ (Scheme S3). Interestingly, we found that the corresponding product was a mixture of deuterium (D) containing 1,4-adducts (**2a'**), in which several deuterium atoms were substituted on the cyclohexyl ring which was determined by ¹H, ¹³C NMR (see NMR spectra), and high resolution mass (HRMS, Fig. S6), while the precise D-substitution position cannot be confirmed. This result indicates that there is an exchange between H from cyclohexyl ring and D from DSiEt₃ on AuPdNPore surface. The result also suggests that the H-Si bond should be cleaved on AuPdNPore surface before the 1,4-addition, and cyclohexenone (**1a**) should be activated by chemisorption on AuPdNPore catalyst as this reviewer commented.

In the presence of the AuNPore catalyst, the disproportionation reaction of cyclohexenone (**1a**) did not proceed at all as shown in Scheme S4. However, the mechanism of the disproportionation of enone catalyzed

by metals is not clear, taking into consideration those supplementary experiment results, we thought that the disproportionation of enone should be related to the hydride species, which may be formed by chemisorption of enone on the Pd of AuPdNPore catalyst.



Scheme S3. Hydrosilylation of **1a** using DSiEt_3 .

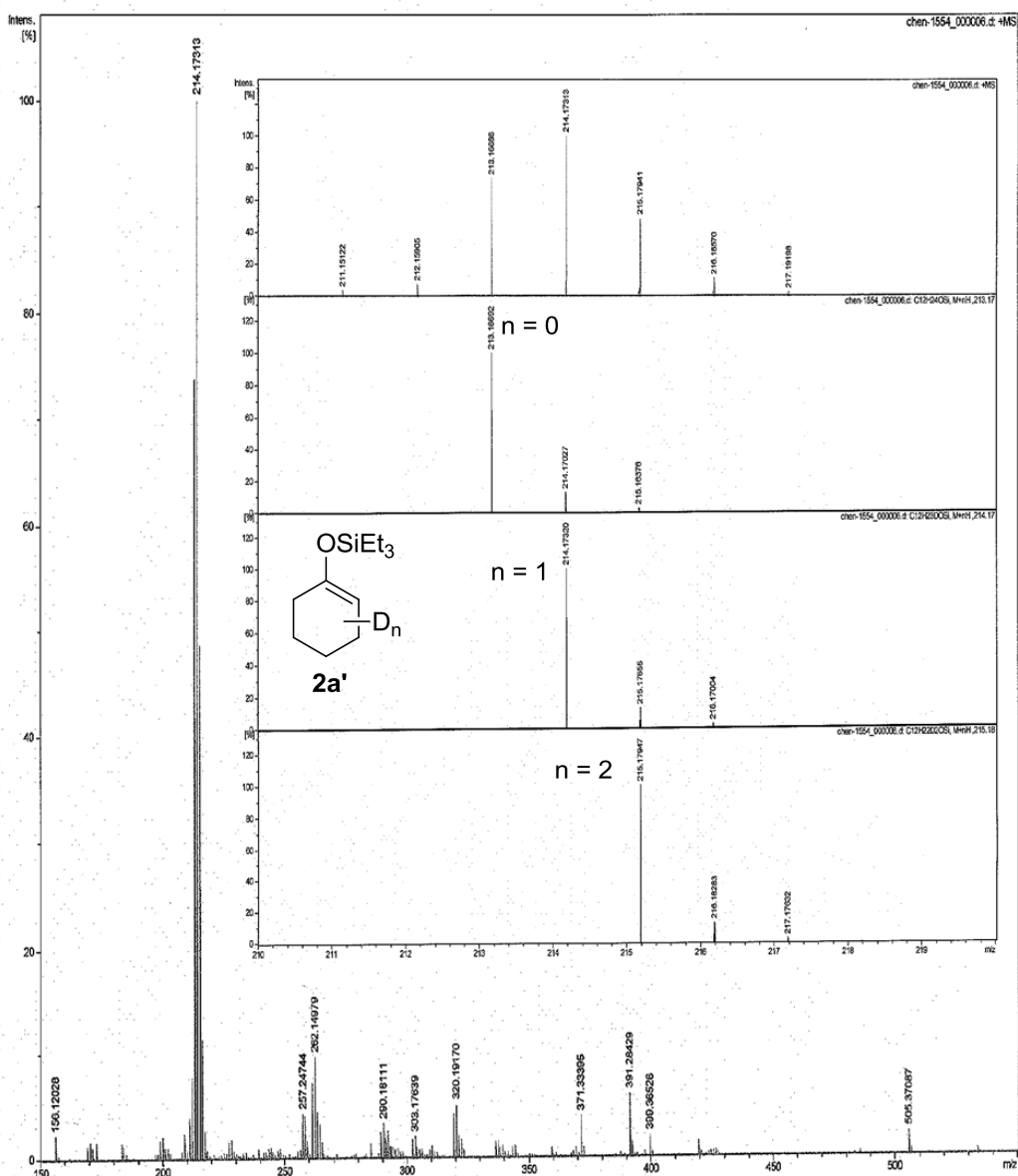
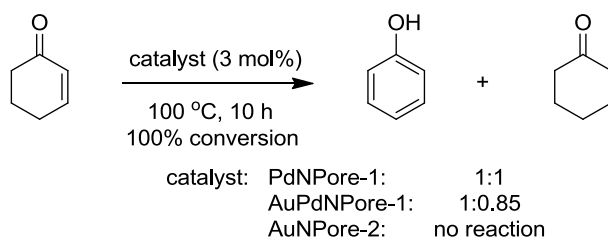


Fig S7. High resolution mass spectra of **2a'**.

Disproportionation reaction without using organosilane



Scheme S4. Disproportionation reactions of 2-cyclohexen-1-one **1a** in the presence of PdNPore-1, AuPdNPore-1, and AuNPore-2, respectively, without using organosilanes.

TEM image of AuPdNPs on TiO₂

AuPdNPs on TiO₂ was fabricated following the reported literature. The average nanoparticle size is about 10 nm. The catalytic activity was shown in Table 1, entry 11 in the text.

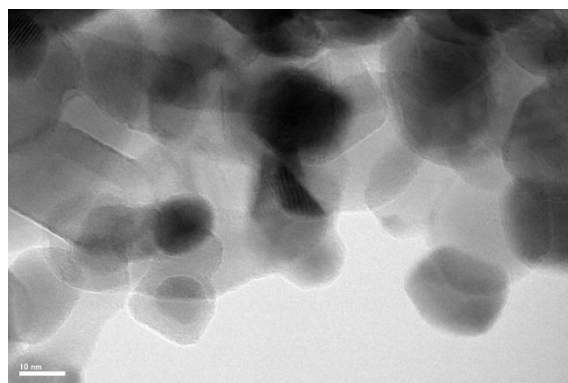
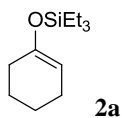


Fig S8 TEM image of AuPdNPs on TiO₂.

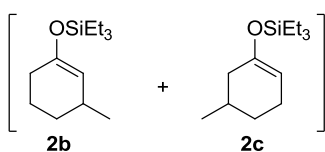
Analysis data

(Cyclohex-1-en-1-yloxy)triethylsilane (**2a**)



Colorless liquid; ¹H NMR (400 MHz, CDCl₃) δ 4.91-4.83 (m, 1H), 2.09-1.93 (m, 4H), 1.71-1.61 (m, 2H), 1.55-1.46 (m, 2H), 0.98 (t, *J* = 8 Hz, 9H), 0.66 (q, *J* = 8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 103.9, 29.9, 23.9, 23.2, 22.4, 6.8, 5.1; HRMS (ESI positive) calcd for C₁₂H₂₄OSi [M+H]⁺: 213.1669, found: 213.1668.

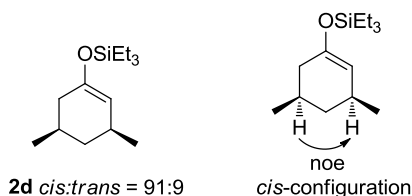
A mixture of triethyl((3-methylcyclohex-1-en-1-yl)oxy)silane (2b) and triethyl((5-methylcyclohex-1-en-1-yl)oxy)silane (2c)



2b + 2c: 0.78-0.74:1

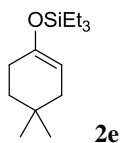
Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.85 (bs, 1H, **2e**), 4.74 (bs, 1H, **2d**), 2.30-2.15 (m, 1H, **2d**), 2.10-1.89 (m, 5H, **2d+2e**); 1.83-1.48 (m, 8H, **2d+2e**), 1.01-0.87 (m, 24H, **2d+2e**), 0.73-0.57 (m, 12H, **2d+2e**); ^{13}C NMR (100 MHz, CDCl_3) δ 150.0, 149.8, 110.6, 103.2, 38.3, 31.2, 30.5, 29.7, 29.5, 29.4, 23.4, 22.5, 21.8, 21.6, 6.7, 5.14, 5.13; HRMS (ESI positive) calcd for $\text{C}_{13}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{H}]^+$: 227.1825, found: 227.1824.

((3,5-Dimethylcyclohex-1-en-1-yl)oxy)triethylsilane (2d)



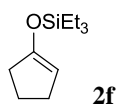
Cis-isomer: colorless liquid; ^1H NMR (600 MHz, CDCl_3) δ 4.70 (bs, 1H), 2.27-2.24 (m, 1H), 1.99-1.96 (m, 1H), 1.74-1.70 (m, 1H), 1.69-1.64 (m, 2H), 1.00-0.92 (m, 15H), 0.74-0.61 (m, 7H); ^{13}C NMR (176 MHz, CDCl_3) δ 149.7, 110.4, 40.8, 38.4, 30.3, 29.7, 22.7, 22.1, 6.8, 5.1; HRMS (ESI positive) calcd for $\text{C}_{14}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 263.1801, found: 263.1800.

((4,4-Dimethylcyclohex-1-en-1-yl)oxy)triethylsilane (2e)



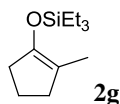
Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.86-4.71 (bs, 1H), 2.12-1.94 (m, 2H), 1.89-1.73 (m, 2H), 1.49-1.35 (m, 2H), 0.98 (t, $J = 8$ Hz, 9H), 0.92 (s, 6H), 0.66 (q, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 102.6, 37.9, 36.0, 28.6, 28.0, 27.5, 6.7, 5.1; HRMS (ESI positive) calcd for $\text{C}_{14}\text{H}_{28}\text{OSi}$ $[\text{M}+\text{H}]^+$: 241.1982, found: 241.1981.

(Cyclopent-1-en-1-yloxy)triethylsilane (2f)



Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 4.62 (bs, 1H), 2.26 (t, $J = 7.2$ Hz, 4H), 1.94-1.77 (m, 2H), 0.98 (t, $J = 8$ Hz, 9H), 0.68 (q, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 155.1, 101.8, 33.5, 28.7, 21.4, 6.6, 4.8; HRMS (ESI positive) calcd for $\text{C}_{11}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{H}]^+$: 199.1512, found: 199.1511.

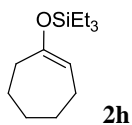
Triethyl((2-methylcyclopent-1-en-1-yl)oxy)silane (2g)



Light yellow liquid; ^1H NMR (400 MHz, CDCl_3) δ 2.37-2.27 (m, 2H), 2.23-2.09 (m, 2H), 1.83-1.74 (m, 2H), 1.60-1.48 (m, 3H), 0.98 (t, $J = 8$ Hz, 9H), 0.65 (q, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 112.8, 34.0, 33.8, 20.0, 12.1, 7.0, 5.7; HRMS (ESI positive) calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 235.1488, found:

235.1487.

(Cyclohept-1-en-1-yloxy)triethylsilane (2h)



Colorless liquid; ^1H NMR (400 MHz, CDCl_3) δ 5.01 (dd, $J = 6.4, 6.4$ Hz, 1H), 2.27-2.21 (m, 2H), 2.01-1.95 (m, 2H), 1.71-1.65 (m, 2H), 1.61-1.48 (m, 4H), 0.97 (t, $J = 7.6$ Hz, 9H), 0.65 (q, $J = 7.6$, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.0, 107.9, 35.5, 31.5, 27.8, 25.4, 25.2, 6.8, 5.0; HRMS (ESI positive) calcd for $\text{C}_{13}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{H}]^+$: 227.1825, found: 227.1824.

NMR spectra

