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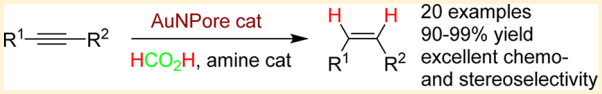
Selective Transfer Semihydrogenation of Alkynes with Nanoporous Gold Catalysts

Yogesh S. Wagh and Naoki Asao*

WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Supporting Information

ABSTRACT: A facile, highly chemo- and stereoselective transfer semihydrogenation of alkynes to *Z*-olefins has been achieved by use of unsupported nanoporous gold (AuNPore) as a heterogeneous catalyst together with formic acid as a hydrogen donor. A variety of terminal/internal and aromatic/aliphatic alkynes were reduced to the corresponding alkenes in high chemical yields with good functional-group tolerance. The catalyst is robust enough to be reused without leaching.

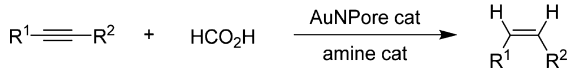


INTRODUCTION

Semihydrogenation of alkynes is one of the most simple and straightforward synthetic methods of alkenes in the laboratory as well as in industry.[1] This transformation has been well established using the Lindlar catalyst with molecular hydrogen, and *Z*-olefins are produced seletively.[2] However, it often suffers from many drawbacks. *E*/*Z* isomerization occurs to a considerable extent. The over-reduction of the produced alkenes to alkanes is a serious problem due to the difficulty of the control of a stoichiometric amount of H_2. The requirement of toxic lead for deactivation of Pd is obviously undesirable. Furthermore, H_2 is highly flammable and readily forms explosive mixtures with air. On the other hand, the catalytic transfer hydrogenation using organic hydrogen donors is attractive because of the operational simplicity and safety.[3] Several protocols with homogeneous catalysts have been reported so far,[4] but heterogeneous catalytic systems are surprisingly quite limited.[5] The first example was reported by Heck in 1978 by use of Pd/C with trialkylammonium formate as a hydrogen source.[5a,b] Johnstone used a combination of Pd-poisoned catalysts with Hg or Pb and sodium phosphinate.[5c] In both cases, however, over-reduction or *E*/*Z* isomerization occurred significantly. Alonso and Yus reported that the nickel nanoparticles were effective for this reaction although substoichiometric amounts of $NiCl_2$ and a large excess of Li metal were required.[5d,e] Cuerva, Cadenas, and Oltra developed a new semihydrogenation system with water as a hydrogen source although excess amounts of Cp_2TiCl were needed.[5f] Liu reported the semihydrogenation with costly Hantzsch ester 1,4-dihydropyridine (HEH) as the hydrogen source.[5g] Furthermore, the recyclability of all these heterogeneous catalysts have not been well investigated. To overcome these limitations, development of a selective and cost-effective heterogeneous catalytic system is highly desirable.

Recently, unsupported nanoporous gold (AuNPore) has emerged as a potentially green and sustainable catalyst in the chemical process, which can be easily obtained from Au alloys by selective leaching of less noble metals, such as Ag, Cu, and Al.[6,7] It has randomly oriented ligaments with a hyperboloid-like shape and nanopore channels, possessing a high density of surface steps and kinks that are active for chemical reactions.[8] Since AuNPore has a high surface area, high stability for versatile chemicals, high reusability, and no toxic nature, it has been successfully applied to the various types of chemical processes in the gas and liquid phases.[9,10] In this context, we recently reported that this material was effective for the transfer semihydrogenation of alkynes.[10h] Unfortunately, however, this method required excess amounts of costly organosilanes as a hydrogen source. Therefore, the formation of stoichiometric amounts of siloxane was inevitable as a byproduct. Also it fails to achieve a higher chemical yield of desired alkenes in some cases. Particularly, the reaction with 1,2-dialkyl-substituted internal alkynes does not go well. In continuation of our interest in this material, we herein report a AuNPore-catalyzed transfer semihydrogenation of alkynes by use of HCO_2H as a hydrogen donor (Scheme 1). With this method, various terminal as well as internal aromatic/aliphatic alkynes were reduced to the corresponding *cis*-alkenes with remarkable stereo- and chemoselectivity in high yields.

Scheme 1. AuNPore-Catalyzed Transfer Semihydrogenation of Alkynes with HCO_2H



RESULT AND DISCUSSION

The transfer semihydrogenation of 4-ethynyl-1,1′-biphenyl (**1a**) was performed under several conditions, and the results are summarized in Table 1. When **1a** was treated with HCO_2H (1 equiv) and Et_3N (1 equiv) in the presence of the AuNPore catalyst (5 mol %) in DMF at 70 °C for 6 h, the reaction proceeded smoothly and the corresponding olefin product (**2a**) was obtained in 99% yield with a trace amount of alkane product (**3a**) (entry 1). The high chemoselectivity was also observed with other solvents, such as THF, CH_3CN, and toluene, although the chemical yield was significantly decreased in the case of CH_3CN

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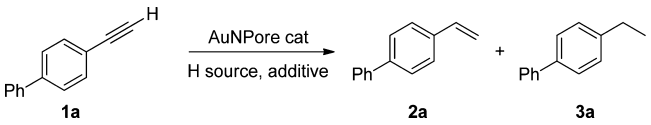
Table 1. Catalytic Transfer Semihydrogenation of Alkyne 1a[a]



1a 2a 3a

entry	solvent	H source	additive	yield (%)[b]	selectivity (2a/3a)
1	DMF	HCO_2H	Et_3N (1 equiv)	99	99/1<
2	THF	HCO_2H	Et_3N (1 equiv)	90	99/1
3	CH_3CN	HCO_2H	Et_3N (1 equiv)	48	100/−
4	toluene	HCO_2H	Et_3N (1 equiv)	35	100/−
5[c]	DMF	HCO_2H	Et_3N (1 equiv)	0	−
6[d]	DMF	HCO_2H	Et_3N (1 equiv)	0	−
7	DMF	H_2 (1 atm)	−	0	−
8[e]	DMF	HCO_2H	Et_3N (0.2 equiv)	98 (98)	99/1<
9[e]	DMF	HCO_2H	Et_3N (0.1 equiv)	90	99/1<

[a]Reaction conditions: **1a** (0.3 mmol), AuNPore (5 mol %), H source (1.0 equiv), additive (0.1−1.0 equiv), 70 °C, 6 h. [b]Determined by ^{1}H NMR analysis with dibromomethane as an internal standard. Isolated yield is shown in parentheses. [c]Reaction was conducted in the absence of AuNPore catalyst. [d]$Au_{30}Ag_{70}$ alloy was used as a catalyst instead of AuNPore. [e]Reaction time is 14 h.

and toluene (entries 2−4). No reactions occurred without AuNPore or with a Au alloy (entries 5−6). It should be noted that H_2 gas (1 atm) is unable to reduce alkynes under the present reaction conditions and the starting material was recovered quantitatively (entry 7). These results clearly indicated that H_2 was not formed from HCO_2H in this chemical process. We found that the reaction proceeded even with 20 mol % of Et_3N, and **2a** was obtained in 98% yield with longer reaction time (14 h) (entry 8).[11] A further decrease of Et_3N to 10 mol % lowered the chemical yield to 90% (entry 9). Based on these results, we decided to use the conditions of entry 8 [(HCO_2H (1 equiv), Et_3N (20 mol %), DMF] as the standard conditions. The substrate generality of the current reaction was examined, and the selected examples are summarized in Table 2. The reaction of phenylacetylene **1b** proceeded much faster than that of **1a** under the standard conditions, and the corresponding product, styrene (**2b**), was obtained after 4 h in 91% yield (entry 1). On the other hand, the reaction of *ortho*-methylphenylacetylene **1c** was sluggish and 8 h were needed for completion, probably due to the steric hindrance of the methyl group at the *ortho*-position (entry 2). Actually, the reactions of *meta*- and *para*-isomers (**1d−e**) finished within 4 h (entries 3−4). Methoxy- and fluoro-substituted phenylacetylene at the *para*-position (**1f−g**) gave the corresponding olefin products (**2f−g**) nearly quantitatively with high selectivity (entries 5−6). Based on the results shown in entries 1 and 4−6, the electronic effect of these substituents on the phenyl ring is negligible. Not only aromatic terminal acetylenes but also aliphatic ones were suitable substrates in the present reaction. For example, propargylbenzene **1h** gave allylbenzene **2h** in 90% yield (entry 7). Furthermore, a variety of functional groups are tolerated in the reaction including nitrile, acetal, and sulphonamide groups (entries 8−10). Interestingly, no over-reduction products were observed with any of the aliphatic alkynes screened (entries 7−10). Next, we conducted the reaction with internal alkynes. When the reaction was performed with diphenylacetylene **1l**, a mixture of *Z*/*E* (95/05) isomers **2l** was produced. To improve the selectivity, further optimization was carried out, and finally the *Z*/*E* selectivity was increased to 100% by use of 1.5 equiv of HCO_2H and 10 mol % of 4-dimethylaminopyridine (DMAP) in DMF as shown in entry 11. However, in the case of phenylbutyne **1m**, the reaction proceeded sluggishly and the corresponding product **2m** was obtained in 75% with the recovery of **1m** in 25% yield even after 36 h. In a further investigation of other hydrogen sources, we found that the use of ammonium formate gave an excellent yield of **2m** with very high selectivity (entry 12). The reaction of dodec-6-yne **1n** also proceeded smoothly with ammonium formate to give *Z*-**2n** as a sole product (entry 13). Since the transfer semihydrogenation of **1n** with R_3SiH did not proceed well, this is a marked contrast result.[10h] Primary propargylic alcohol **1o** was also hydrogenated efficiently to *Z*-cinnamyl alcohol **2o** (entry 14). Benzyl ethers are vulnerable for hydrogenolysis of the benzyl group under hydrogenation reaction conditions (H_2/Pd−C). The present transfer semihydrogenation using the AuNPore catalyst allows us to selectively reduce the alkyne of benzyl protected propargyl alcohol **1p** without disturbing the benzyl group providing excellent selectivity for *Z*-olefin (entry 15). The selective semihydrogenation was also successfully achieved with electron-deficient internal alkynes **1q−t**, bearing electron-withdrawing groups, such as nitrile, ketone, and ester groups, and the corresponding olefin products **2q−t** were obtained in nearly quantitative yields with excellent chemo- and stereoselectivity (entries 16−19). With the reactivity of alkene for over-reduction noted, the hydrogenation reaction of *cis*-stilbene **2l** was performed under the present reaction conditions (same as Table 2, entry 11). As expected, no reaction occurred and **2l** was recovered quantitatively. This result reveals that the present method is highly selective for semihydrogenation of alkynes.

We next examined the split test to clarify whether the AuNPore-catalyzed reaction proceeds heterogeneously or not. The reaction of **1a** was performed under the standard conditions for 6 h. At this stage, **2a** was formed in 40% yield. Then, half of the supernatant solution was transferred to another reaction vessel, and it was stirred for a further 10 h in the absence of the catalyst. As we expected, the amount of **2a** remained unchanged in the supernatant. In contrast, the reaction of the residual mixture containing the AuNPore catalyst gave **2a** in 98% yield after 10 h (Scheme 2). Furthermore, only a negligible amount of gold leaching (4.7 ppb) into the reaction mixture was detected by inductively coupled plasma mass spectrometry (ICP-MS) analysis. These results clearly indicated that the current reaction proceeded through a heterogeneous process. The catalyst can be recovered easily by just filtration without any cumbersome separation technique such as centrifugation, and it can be reused repeatedly. When the reaction of **1e** was conducted five times, the corresponding olefin product **2e** was obtained in high yield every time (Figure 1). SEM analysis revealed that the nanostructure of the catalyst was not changed at all even after five uses (Figure S1 in the Supporting Information).

■ CONCLUSION

In summary, we have established for the first time that the AuNPore is an effective and reusable catalyst for the transfer semihydrogenation of various terminal as well as internal aromatic/aliphatic alkynes by use of HCO_2H, leading to *Z*-olefins in high yields with excellent chemo- and stereoselectivity. HCO_2H is a cost-effective and easily available hydrogen source. A variety of reducible functional groups are tolerated in the reaction including nitrile, ketone, and ester groups. Further studies to elucidate the mechanism of the current transformation and to extend the scope of the synthetic utility are in progress in our laboratory.

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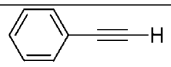
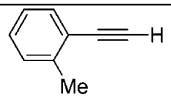
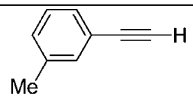
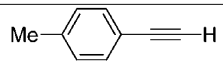
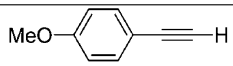
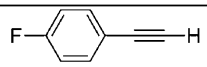
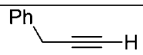
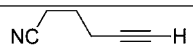
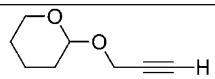
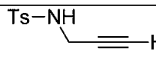
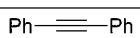
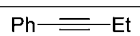
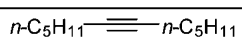
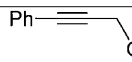
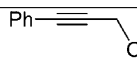
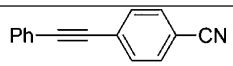
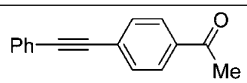
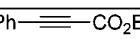
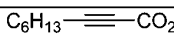
Table 2. AuNPore-Catalyzed Transfer Semihydrogenation of Alkynes[a]

entry	alkyne		time (h)	yield (%)[b]	selectivity (alkene/alkane)
1		**1b**	4	91	100/-
2		**1c**	8	92	98/2
3		**1d**	4	93	99/1
4		**1e**	4	96	99/1
5		**1f**	4	99	99/1
6		**1g**	5	98	100/-
7		**1h**	4	90	100/-
8		**1i**	4	96	100/-
9		**1j**	5	98	100/-
10		**1k**	5	99 (98)	100/-
11[c]		**1l**	4	99 (96)	100/-[d]
12[e]		**1m**	11	99 (96)	100/-[f]
13[e]		**1n**	19	99 (98)	100/-[d]
14[c]		**1o**	2	99 (95)	100/-[d]
15[e]		**1p**	19	98 (95)	100/-[f]
16[c]		**1q**	4	99 (98)	100/-[d]
17[c]		**1r**	4	99 (98)	100/-[d]
18[c]		**1s**	2	99 (95)	100/-[d]
19[c]		**1t**	1	99 (94)	100/-[d]

[a]Reaction conditions: alkyne (0.3 mmol), AuNPore (5 mol %), HCO_2H (0.3 mmol), Et_3N (20 mol %), DMF, 70 °C. [b]Determined by ^1H NMR using dibromomethane as an internal standard. Isolated yield is shown in parentheses. [c]HCO_2H (0.45 mmol), DMAP (10 mol %). [d]Z/E ratio was 100:0. [e]HCO_2NH_4 (0.3 mmol) was used instead of HCO_2H/Et_3N in CH_3CN (0.5M) at 80 °C. [f]Z/E ratio was 99:1.

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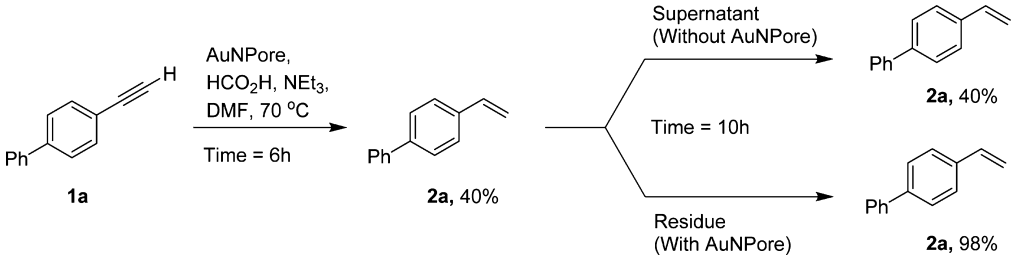
Scheme 2. Leaching Experiment by Split Test for AuNPore Catalyzed Transfer Semihydrogenation of 1a



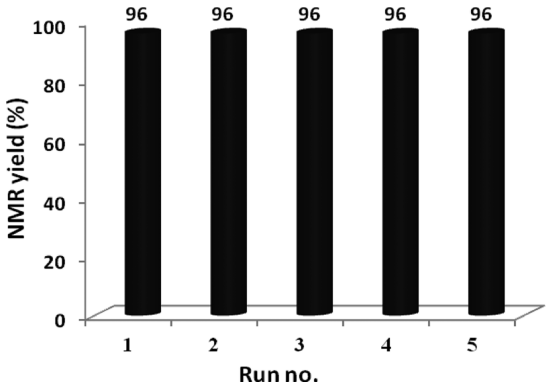


Figure 1. Reusability of AuNPore for transfer semihydrogenation of **1e**.

EXPERIMENTAL SECTION

General Information. Scanning electron microscope (SEM) observation was carried out at an accelerating voltage of 30 kV. EDX analysis was carried out at an accelerating voltage of 20 kV. All the reactions were carried out under a nitrogen atmosphere. The progress of the reaction was monitored on GC-MS/TLC. GC-MS analysis was performed on GC interfaced to a mass-selective detector (30 m × 0.25 mm capillary column, HP-5MS). NMR spectra were measured at 400 MHz for ^{1}H and 100 MHz for ^{13}C. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40−100 μm).

Materials. The commercially available alkynes are used as received. Alkyne **1k**,[12a] **1p**,[12b] **1q**,[12c] and **1r**[12c] were prepared following the reported literature procedure. The chemical yield of all products was determined by ^{1}H NMR analysis with dibromomethane as an internal standard. All the products are known, and their spectral data are consistent with previously published literature values.

Preparation Procedure of AuNPore Catalysts. Au (99.99%) and Ag (99.99%) were melted with an electric arc-melting furnace under an argon atmosphere to form Au/Ag alloy (30:70, in at.%), which was rolled down to a thickness of 40 μm. The foil was annealed at 850 °C for 18 h in the electrical muffle furnace. The resulting foil was cut into small pieces (2 × 2 mm^2 square). Immersion of the many resulting chips (total weight: 50 mg) in an excess amount of 70 wt % nitric acid (50 mL) for 18 h at room temperature resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with saturated aq. $NaHCO_3$, distilled water, and acetone, successively. Drying of the material under reduced pressure gave the AuNPore (22.1 mg), and its composition was determined to be $Au_{99.24}Ag_{0.76}$ by EDX analysis.

Representative Procedure for the AuNPore-Catalyzed Transfer Semihydrogenation of Terminal Alkyne 1a (Table 1, entry 8). To a V-shaped vial reactor containing AuNPore (3.0 mg, 5 mol %) and **1a** (53.4 mg, 0.3 mmol) were added DMF (1 M, 0.3 mL), HCO_2H (11.3 μL, 0.3 mmol), and NEt_3 (8.4 μL, 20 mol %) subsequently at room temperature. The reaction mixture was stirred at 70 °C for 14 h and was monitored by TLC and GC-MS. The AuNPore catalyst was recovered by filtration, and the solution was extracted with ethyl acetate. After the organic layer was washed with water (20 mL × 3), the organic solvent was evaporated under reduced pressure to give a crude material. The crude material was purified with silica gel chromatography to afford **2a** (53 mg, 98%) as a white solid. All the following products are known, and spectral data are consistent with those of authentic samples or previously published literature values: **2a**,[10h] **2b**, **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2k**.[10h] Spectral data for some selected compounds are given below.

*4-Vinyl-1,1′-biphenyl (**2a**).* White solid, 52 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.57 (m, 4H), 7.5−7.43 (m, 4H), 7.37−7.33 (m, 1H), 6.77 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.8 (d, *J* = 17.6 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H).

*N-Allyl-4-methylbenzenesulfonamide (**2k**).* White solid, 62 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.7 (d, *J* = 8.4 Hz, 2H), 7.27−7.21 (m, 2H), 5.7−5.61 (m, 1H), 5.13−5.01 (m, 2H), 4.84−4.81 (m, 1H), 3.54−3.5 (m, 2H), 2.37 (s, 3H).

Representative Procedure for the AuNPore-Catalyzed Transfer Semihydrogenation of Internal Alkyne 1l (Table 2, entry 11). To a V-shaped vial reactor containing AuNPore (3.0 mg, 5 mol %), **1l** (53.4 mg, 0.3 mmol), and DMAP (3.66 mg, 10 mol %) were added DMF (1 M, 0.3 mL) and HCO_2H (17 μL, 0.45 mmol) subsequently at room temperature. The reaction mixture was stirred at 70 °C for 4 h and was monitored by TLC and GC-MS. The AuNPore catalyst was recovered by filtration, and the solution was extracted with diethyl ether. After the organic layer was washed with water (20 mL × 3), the organic solvents were evaporated under reduced pressure to give a crude material. The crude material was purified with silica gel chromatography to afford **2l** (52 mg, 96%) as a colorless liquid. All the following products are known, and spectral data are consistent with those of authentic samples or previously published literature values: **2l**, **2m**,[12d] **2n**,[12e] **2o**,[12f] **2p**,[12f] **2q**,[12g] **2r**,[12g] **2s**,[12g] and **2t**.[10h] Spectral data for some selected compounds are given below.

*(Z)-1,2-Diphenylethene (**2l**).* Colorless liquid, 52 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.16 (m, 10H), 6.6 (s, 2H).

*(Z)-But-1-en-1-ylbenzene (**2m**).* Colorless liquid, 38 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.19 (m, 5H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.68−5.62 (m, 1H), 2.39−2.31 (m, 2H), 1.06 (t, *J* = 7.6 Hz, 3H).

*(Z)-Dodec-6-ene (**2n**).* Colorless liquid, 49.4 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.36 (t-like m, *J* = 4.8 Hz, 2 H), 2.05−2.0 (m, 4 H), 1.38−1.27 (m, 12 H), 0.90 (t, *J* = 6.8 Hz, 6 H).

*(Z)-3-Phenylprop-2-en-1-ol (**2o**).* Colorless liquid, 38 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.19 (m, 5H), 6.57 (d, *J* = 11.6 Hz, 1H), 5.87 (dt, *J* = 11.6, 6.4 Hz, 1H), 4.45−4.43 (m, 2H), 1.59−1.55 (bs, 1H).

*(Z)-3-(Benzyloxy)prop-1-en-1-yl)benzene (**2p**).* Colorless liquid, 64 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.19 (m, 10H), 6.62 (d, *J* = 12 Hz, 1H), 5.94−5.88 (m, 1H), 5.53 (s, 2H), 4.2 (dd, *J* = 6, 1.2 Hz, 2H).

*(Z)-3-Styrylbenzonitrile (**2q**).* White solid, 60 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8 Hz, 2H), 7.31 (d, *J* = 8 Hz, 2H), 7.27−7.17 (m, 5H), 6.75 (d, *J* = 12.4 Hz, 1H), 6.56 (d, *J* = 12.4 Hz, 1H).

*(Z)-1-(3-Styrylphenyl)ethan-1-one (**2r**).* White solid, 65 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8 Hz, 2H), 7.26−7.21 (m, 5H), 6.73 (d, *J* = 12.4 Hz, 1H), 6.61 (d, *J* = 12.4 Hz, 1H), 2.57 (s, 3H).

*Ethyl-(Z)-3-phenyl Acrylate (**2s**).* Colorless liquid, 50 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.56 (m, 2H), 7.37−7.31 (m, 3H), 6.94 (d, *J* = 12.8 Hz, 1H), 5.94 (d, *J* = 12.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).

*Methyl-(Z)-non-2-enoate (**2t**).* Colorless liquid, 48 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26−6.19 (m, 1H), 5.6 (dt, *J* = 11.6,

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2 Hz, 1H), 3.69 (s, 3H), 2.67−2.61 (m, 2H), 1.45−1.39 (m, 2H), 1.36−1.28 (m, 6H), 0.87 (t, J = 6.8 Hz, 3H).

Procedure for Leaching Experiment by Split Test (Scheme 2). To a V-shaped vial reactor containing AuNPore (10.0 mg, 5 mol %) and **1a** (178 mg, 1.0 mmol) were added DMF (1 M, 1 mL), HCO_2H (38 μL, 1.0 mmol), NEt_3 (28 μL, 20 mol %) and 1, 3, 5-trimethoxybenzene (16.8 mg, 0.1 mmol, internal standard) subsequently at room temperature. The reaction mixture was stirred at 70 °C for 6h. At this stage, 10 μL of the supernatant solution was picked up for checking the chemical yield of **2a** with ^{1}H NMR (40%). Then, 0.5 mL of the supernatant was transferred to vessel-2, and it was stirred for 10 h at 70 °C in the absence of the catalyst. The chemical yield of **2a** was checked again by picking up 10 μL of the resulting solution and it remain unchanged (40%). In contrast, the residual containing the AuNPore catalyst was completed in 10 h, giving **2a** in 98% ^{1}H NMR yield.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: asao@m.tohoku.ac.jp.

Notes

The authors declare no competing financial interest.

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(11) When the reaction of **1a** was carried out with the AuNPore ($Au_{98}Ag_2$) catalyst prepared in ref 10h instead of the current catalyst ($Au_{99.24}Ag_{0.76}$), the corresponding product **2a** was obtained in 50% yield under the same reaction conditions with entry 8 of Table 1.

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