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Aerobic Oxidation of Amines Catalyzed by Polymer-Incarcerated Au Nanoclusters: Effect of Cluster Size and Cooperative Functional Groups in the Polymer

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Aerobic oxidation reaction of amines to imines catalyzed by polymer-incarcerated Au nanoclusters (PI-Au) was developed. The effect of cluster size for this oxidation reaction was carefully examined using the same polymer support. We have succeeded in preparation of various PI-Au catalysts containing different size clusters by modification of standard preparation methods. The size of clusters and their distribution were analyzed by electron microscopy. Interestingly, catalysts containing relatively larger clusters (>5 nm) showed higher activity in aerobic oxidation of amines than catalysts containing smaller clusters (1–3 nm) that showed much better activity for aerobic oxidation of alcohols. In addition, novel Au nanocluster catalysts immobilized on newly prepared polymer with tertiary amine groups were developed and they showed excellent activity for aerobic oxidation of amines to imines. The relation between cluster size and catalytic activity and role of tertiary amine in polymer were discussed. These catalysts could be applied to aerobic oxidative deprotection of *p*-methoxybenzyl groups.

Since Haruta's discovery, aerobic oxidation reactions catalyzed by gold nanoclusters have been widely investigated.[1,2] There are two important factors for the activity of gold nanocluster catalysts, cluster size and a support.[2–4] Cluster size affects the activity of the catalysts by both surface area and quantum size effect.[4,5] Cluster size is also influenced by the support, and some metal oxide supports can activate Au clusters by electronic effects. In other cases, the support itself sometimes works as a cocatalyst with Au clusters.[4,6] In general, smaller clusters show higher activity than larger clusters because of their high surface area to volume ratio. Moreover, the catalytic activity normalized by the number of surface atoms of smaller Au cores is known to be higher than that of larger clusters in the oxidation of CO, glucose, and alcohols.[4,5]

Recently, aerobic oxidation of amines to imines catalyzed by various sizes of Au, such as bulk, microsize, nanosize, and homogeneous Au, have been widely reported.[7] Interestingly, 10–50 nm size Au clusters sometimes show very high activity in these reports,[7g–7i] although over 10 nm Au clusters hardly catalyze other aerobic oxidation reactions. In some cases in this amine oxidation, it was concluded that smaller Au clusters have higher activity;[7d,7h] however, there is no clear and direct evidence that smaller clusters have higher activity for aerobic oxidation of amines to imines because there are no reports that compare systematically the activity of different sizes of Au clusters using the same support.

We recently reported that gold nanocluster catalysts immobilized on polystyrene-based polymers with crosslinking moieties,[8] polymer-incarcerated gold nanocluster catalysts (PI-Au), were effective for aerobic oxidation of alcohols to ketones, aldehydes, and esters and hydroquinones to quinones under mild conditions.[9,10] Moreover, PI-Au could be reused several times by simple operations without loss of catalytic activity.

We now report aerobic oxidation of amines to imines catalyzed by PI-Au. Comparison of catalytic activity using different size Au clusters in the same polymer support with different preparation methods is described. A novel Au cluster catalyst immobilized on newly designed polymers with cooperative functional groups for this reaction is also described.

Results and Discussion

Preparation of Catalysts. PI-Au catalysts were prepared following a previously reported method (Scheme 1).[9a] As the loading level increased, the ratio of the loaded Au to the used Au source decreased, probably because of saturation.

Oxidation of Dibenzylamine Catalyzed by PI-Au with Different Au Loadings. We have already shown the

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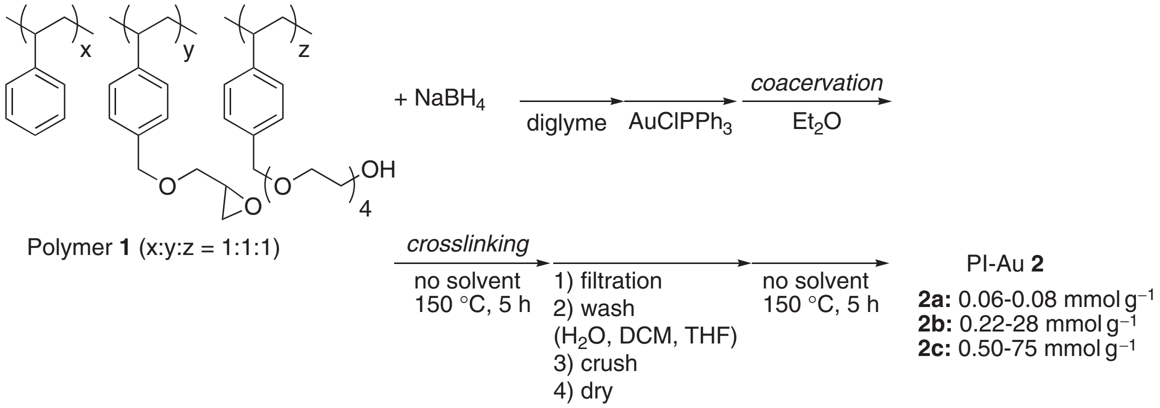
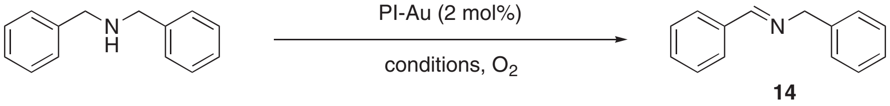


Scheme 1. Preparation of PI-Au catalysts.

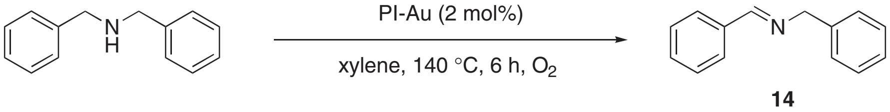
Table 1. Aerobic Oxidation of Dibenzylamine Catalyzed by PI-Au Catalysts with Different Loadings



Conditions	Use	Loading: 0.078 mmol g^{-1} PI-Au **2a** yield/%[a)]	Loading: 0.25 mmol g^{-1} PI-Au **2b** yield/%[a)]	Loading: 0.59 mmol g^{-1} PI-Au **2c** yield/%[a)]
100 °C, 24 h, toluene	1st	10	28	46
	2nd	30	36	54
	3rd	27	39	47
140 °C, 24 h, xylene	1st	92	98	97
	2nd	77	100	100
	3rd	94	98	98

a) Determined by GC analysis.

Table 2. Evaluation of Catalytic Activity before and after Using for Amine Oxidation



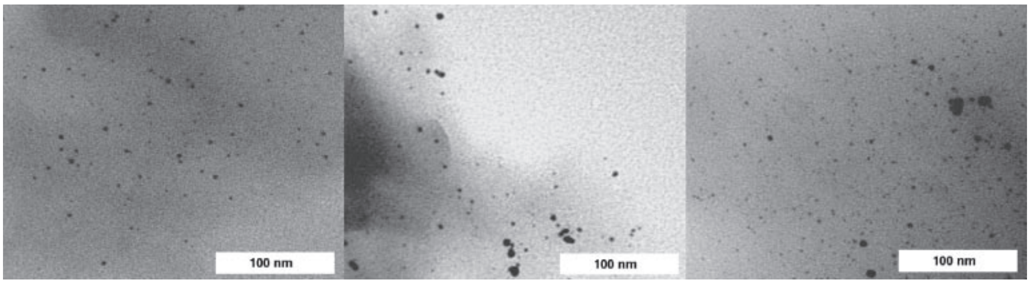
	Yield[a)]/% [PI-Au **2a**]	Yield[a)]/% [PI-Au **2c**]
Fresh	18	73
After three sets of use	74	89

a) Determined by GC analysis.

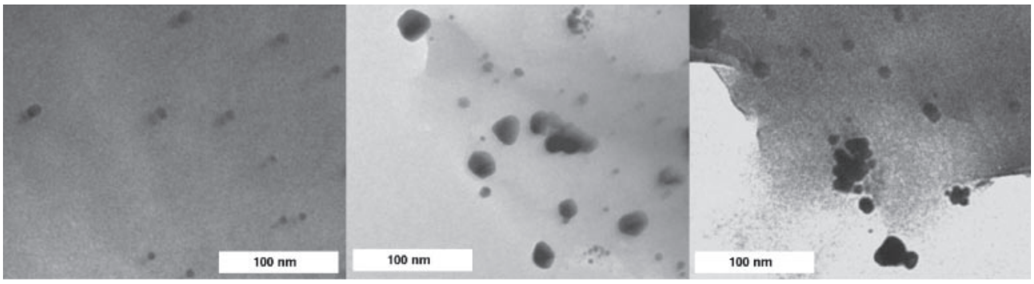
relationship among loading level, cluster size, and activity of PI-Au at room temperature in alcohol oxidation.[9a] When the loading level of the catalyst was low (0.05–0.10 mmol g^{-1} Au), smaller clusters were observed and the catalyst showed higher activity in aerobic oxidation of alcohols. On the other hand, when the loading level was high ($>$0.20 mmol g^{-1}), larger clusters were observed and the catalyst showed lower activity.

We investigated aerobic oxidation of benzylamine using three catalysts with different loadings (PI-Au **2a** 0.078, **2b** 0.25, and **2c** 0.59 mmol g^{-1}) under two different conditions (Table 1: 100 °C, 24 h, in toluene; 140 °C, 24 h, in xylene). Under the latter conditions, all catalysts gave the desired imine in excellent yields, and no decrease of the catalytic activity was observed during three sets of recovery and reuse. On the other hand, under milder conditions at 100 °C, the results differed greatly depending on the loadings of the catalysts. Interestingly, the higher loading catalyst PI-Au **2c** showed good catalytic activity although the lower loading catalyst PI-Au **2a**, which showed excellent activity in aerobic oxidation of alcohols, hardly catalyzed this reaction. Moreover, the recycled catalyst surprisingly showed higher activity than the initial catalyst in the cases of catalysts PI-Au **2a** and **2b**.

Effect of Recycling on Oxidation of Dibenzylamine Catalyzed by PI-Au. To discover the reason, we evaluated the catalytic activity of catalysts with high and low Au loading 1) before use and 2) after three sets of use under 140 °C, 24 h, in xylene for the catalysts (Table 2). When the reaction time was short under these conditions, 140 °C, 6 h, in xylene, only 18% yield of the imine was obtained using fresh PI-Au **2a**. In contrast, the catalyst after being used three times for aerobic



PI-Au **2a** before use PI-Au **2b** before use PI-Au **2c** before use



PI-Au **2a** after 3 uses PI-Au **2b** after 3 uses PI-Au **2c** after 3 uses

Figure 1. Typical TEM images of PI-Au before and after use for amine oxidation.

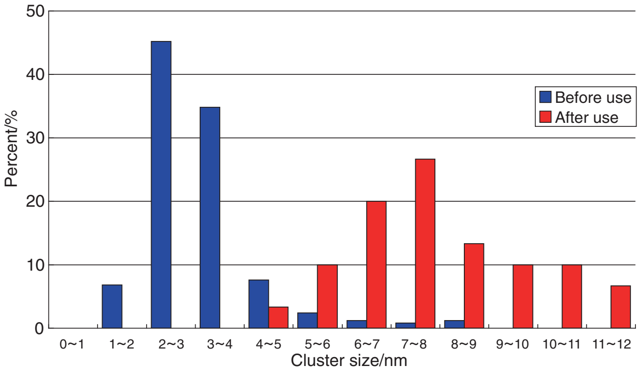


Figure 2. Size distribution of PI-Au **2a** before and after use for amine oxidation.

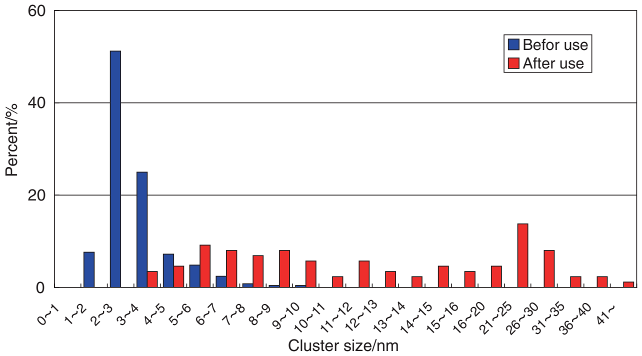


Figure 3. Size distribution of PI-Au **2b** before and after use for amine oxidation.

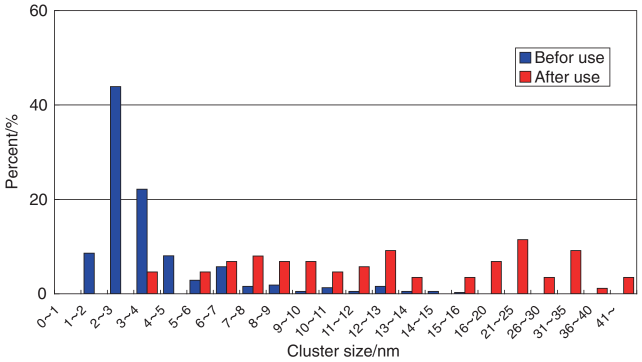


Figure 4. Size distribution of PI-Au **2c** before and after use for amine oxidation.

oxidation of dibenzylamine under 140 °C, 24 h, in xylene, showed rather good activity. In the case of PI-Au **2c**, the activity of the catalyst increased after recycling, however the difference was less dramatic than in the case of the low-loading catalyst.

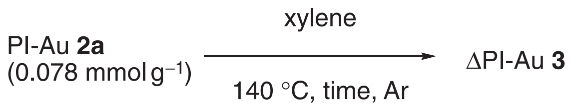
Transmission electron microscopy (TEM) analysis revealed that the cluster size of the recycled catalyst was increased by aggregation of the clusters (Figure 1). In the case of PI-Au **2a**, the range of cluster size changed from 1 to 10 nm (average: 3.0 nm) to 4–12 nm (average: 6.9 nm) with a comparatively narrow distribution (Figure 2). On the other hand, in the cases of PI-Au **2b** and **2c**, the range of cluster sizes in the initial catalyst was 1–10 (average: 3.2 nm) and 1–16 nm (average: 3.8 nm), respectively, which changed to 3–41 (average: 14.3 nm) and 3–50 nm (average: 16.0 nm), respectively, after three sets of use in amine oxidation reactions (Figures 3 and 4).

Based on these results, we formed a working hypothesis that clusters with a size over 5 nm possess higher reactivity for aerobic oxidation of amines than those with a size around 1–3 nm, which are generally highly active for aerobic oxidation of alcohols.

Effect of Preheating on Reactivity and Cluster Size. PI-Au **2a** with 0.078 mmol g^{-1} Au loading was heated in xylene at

140 °C for different periods under Ar, and we studied the relationship among heating time, cluster size and activity for the dibenzylamine oxidation reaction (Scheme 2 and Table 3). The average cluster size was correlated with heating time, and larger cluster size was obtained by longer heating time. It is noted that reactivity also increased as the size of the clusters increased.

Another approach to obtain PI-Au catalysts with larger clusters was to heat polymer microcapsules in an appropriate solvent in the process of crosslinking. We prepared PI-Au **4** and **5** by crosslinking in mesitylene and decane at 150 °C, respectively, and tested them in amine oxidation reactions (Scheme 3). As a result, PI-Au **4** crosslinked in mesitylene had an average cluster size of 6.6 nm and showed high activity even with low loading of Au (Figures 5 and 6). PI-Au **5** crosslinked in decane had an average cluster size of 8.5 nm and showed high activity. When these catalysts were applied to the aerobic oxidation of an alcohol, the activity was in inverse proportion to the activity of amine oxidation (Table 4). Therefore, it was clarified that an important factor for oxidation of amines is not Au loading but cluster size.



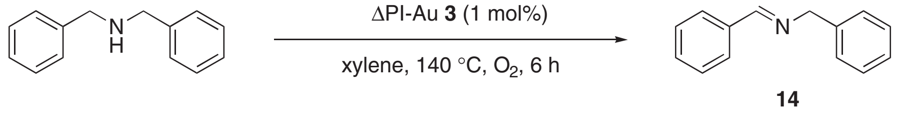
Scheme 2. Activation of PI-Au **2a** by heating.

Based on these results, when polymer **1** was used as a support, apparently the optimum cluster size for aerobic oxidation of amines was larger than that for oxidation of alcohols.

Effect of a Functional Group in the Polymer on Reactivity and Cluster Size. Next, we changed the polymer structure from polymer **1** to **6**, which contains an amine moiety (Figure 7). The preparation method follows that of PI-Au **4**, crosslinking being conducted in mesitylene to afford PI-Au **7** (Scheme 4). The distribution of cluster sizes was measured by scanning transmission electron microscopy (STEM) analysis, and it was found that the average cluster size was 5.0 nm and the median cluster size was 5 to 6 nm. This size distribution was quite similar to that of PI-Au **4** (Figures 8 and 9).

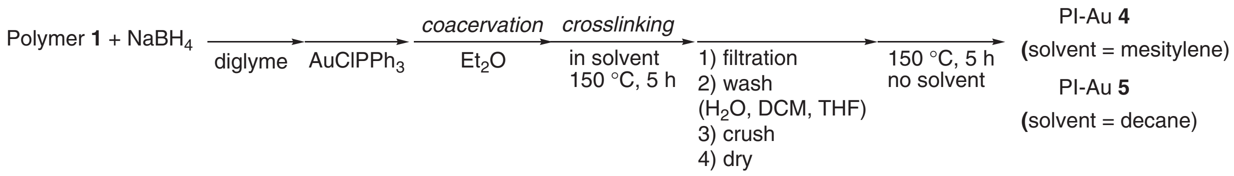
Catalytic activities of PI-Au **2a**, **2c**, **4**, and **7** were compared in the aerobic oxidation of an amine at various temperatures (Table 5). PI-Au **2a** and **2c** showed good activity at 140 °C, however the reaction was sluggish at 100 °C. On the other hand, PI-Au **4** and **7** smoothly worked at 100 °C. This is

Table 3. Relationship among Reactivity, Heating Time, and Cluster Size



Preheating time/h	0	0.5	1	3	8	24	72	150
Yield/%[a]	40	38	40	41	45	52	57	61
Average cluster size/nm	3.0			3.0		3.5	4.1	

a) Determined by GC analysis.



Scheme 3. Preparation of PI-Au **4** and **5**.

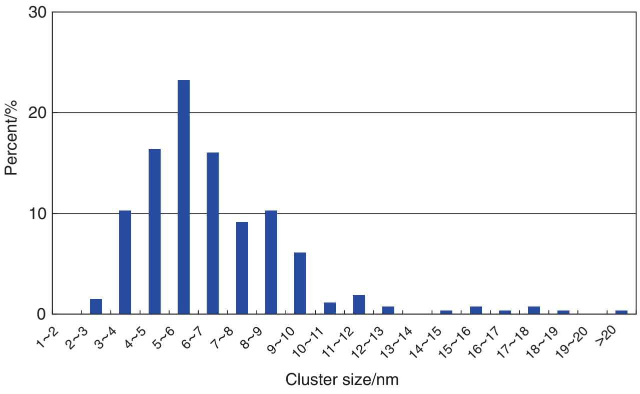


Figure 5. Size distribution of PI-Au **4**.

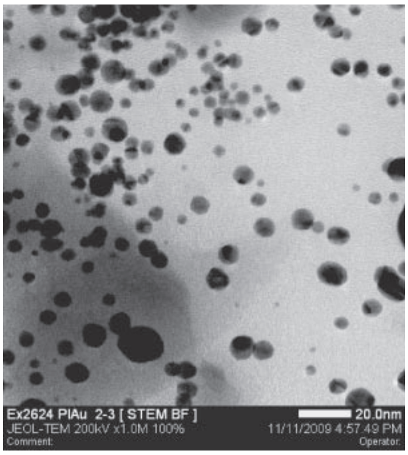
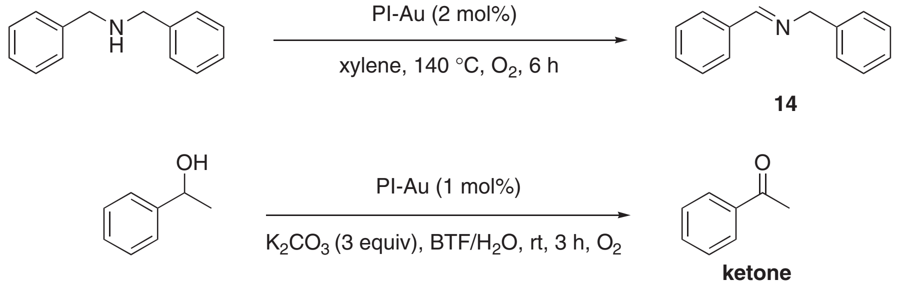


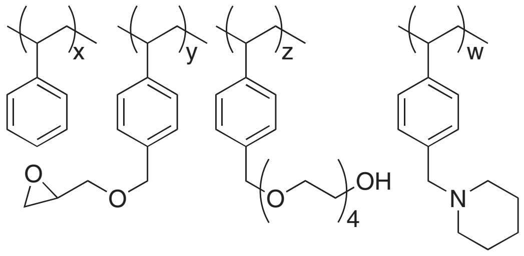
Figure 6. Typical STEM image of PI-Au **4**.

Table 4. Evaluation of Catalytic Activity of PI-Au **4** and **5** and Their Loadings and Cluster Sizes



Entry	PI-Au	Cluster size /nm[b)]	Loading /mmol g^{-1}	Yield of **14** /%[a)]	Yield of **ketone** /%[a)]
1	**2a**	3.0	0.078	40	>90
2	**2c**	3.8	0.59	84	56
3	**4**	6.6	0.072	94	5
4	**5**	8.5	0.069	90	8

a) Determined by GC analysis. b) Average value.

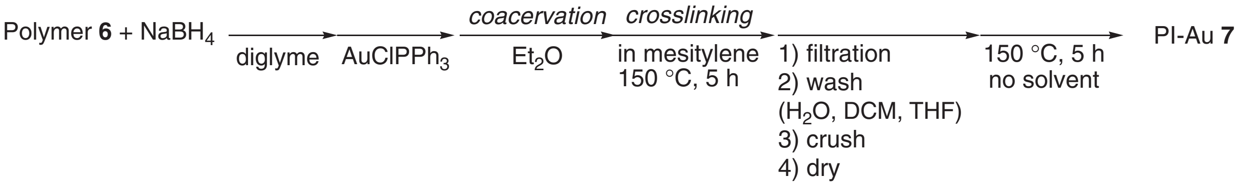


Polymer **6** (x:y:z:w = 6:6:6:1)

Figure 7. Polymer containing a tertiary amine group.

because Au clusters in PI-Au **2a** and **2c** could aggregate and be activated at 140 °C, but not at 100 °C. It should be noted that PI-Au **7** gave a satisfactory result even at 80 °C.

Relationship among Reactivity, Cluster Size, and Functional Groups in the Polymer. Judging from the results in Table 2 and Figures 2–5, the recycled catalyst that contained larger Au clusters (over 5 nm) showed higher activity for amine oxidation than the initial catalysts with 2–4 nm clusters on average. However, the size distributions of the recycled catalysts in Table 2 were too scattered to determine the best range of cluster size. On the other hand, PI-Au **4** and **7**, which were crosslinked in mesitylene, showed relatively narrow size distributions of Au clusters between 4 and 7 nm on average and



Scheme 4. Preparation of PI-Au **7**.

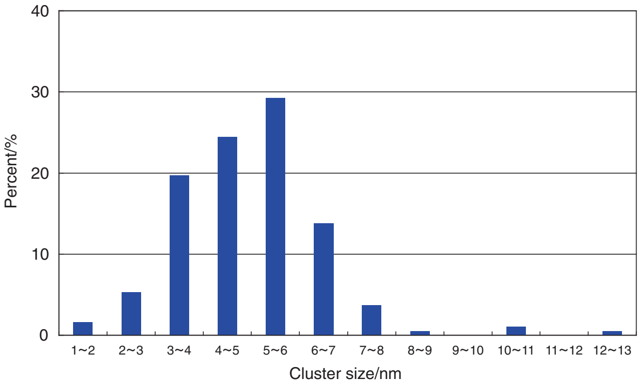


Figure 8. Size distribution of PI-Au **7**.

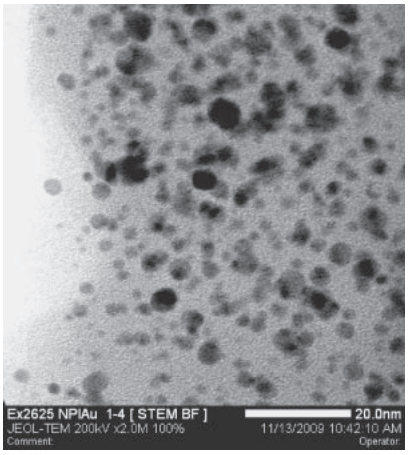
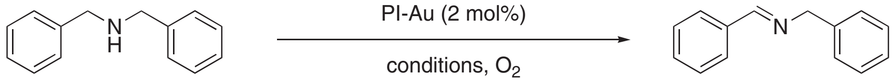


Figure 9. Typical STEM image of PI-Au **7**.

Table 5. Comparison of Catalytic Activities of PI-Au **2a**, **2c**, **4**, and **7** under Various Conditions



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PI-Au conditions	Yield/%			
	2a	**2c**	**4**	**7**
Toluene, 80 °C, 20 h[a]	—	—	40	54[c] (83)[b,c]
Toluene, 100 °C, 12 h[a]	—	—	73	88[c]
Toluene, 100 °C, 24 h[a]	10	46	—	—
Xylene, 140 °C, 6 h[a]	—	84	94	—
Xylene, 140 °C, 24 h[a]	92	97	—	—

a) Yield was determined by GC analysis. b) With 5 mol % of PI-Au for 42 h. c) No Au leaching was confirmed by ICP analysis (<0.04%).

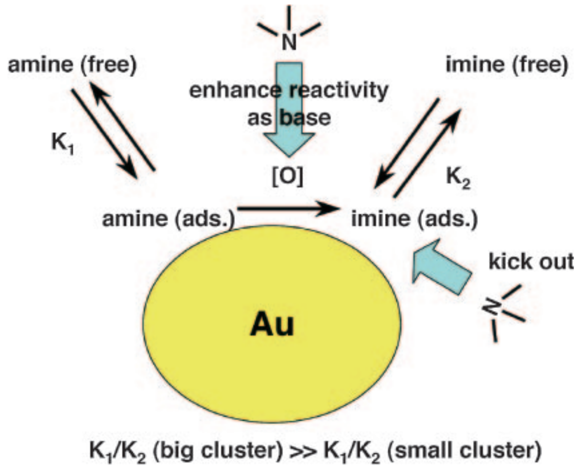


Figure 10. Assumed mechanism of aerobic oxidation of amines on a gold nanocluster.

their reactivity for the amine oxidation was higher than that of PI-Au **2a** and **2c** both before and after recycling.

While average cluster size and distribution are not so different among PI-Au with 0.078 mmol g^{-1} **2a**, 0.25 mmol g^{-1} **2b**, and 0.59 mmol g^{-1} **2c**, the activity of the amine oxidation at 100 °C for 24 h was very different from the reaction at 140 °C for 6 h. We already confirmed that aggregation of Au clusters hardly occurred without solvent even at 170 °C.[9a] In contrast, Au clusters aggregated easily at 140 °C for all loading levels of catalysts in the presence of a solvent that swelled the polymer, because crosslinked polymer fixed small Au clusters less tightly and Au clusters could move to aggregate in swelled polymer with solvents. Au clusters easily aggregated to form larger clusters in the catalyst with higher loading, because the concentration of clusters was higher and clusters could encounter each other with shorter moving distances. On the other hand, when a catalyst was heated in an appropriate solvent just after microencapsulation in the crosslinking step (PI-Au **4** and **5**), larger clusters that showed higher reactivity could be obtained even for low-loading catalysts, probably because Au clusters could move more freely inside the polymer before extensive crosslinking (Scheme 3 and Table 4, Entries 3 and 4).

We thought that the relationship between the cluster size and the reactivity could be explained by a balance of adsorption of substrates and products because relative adsorption strength of imines against amines on small clusters, K_1/K_2 (small cluster), might be larger than that on large clusters, K_1/K_2 (big cluster) (Figure 10).

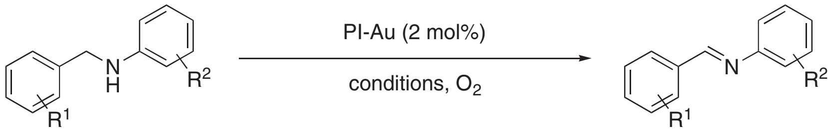
Another factor to improve the catalytic activity was the introduction of a tertiary amine group in the polymer (Figure 7). Although the size distribution and average cluster size of PI-Au **4** and **7** were similar (Figure 8), PI-Au **7**, which was immobilized on polymer with a tertiary amine, showed higher activity, especially at lower temperature than PI-Au **4**.

One of the effects of a tertiary amine in the polymer may be explained by its role as a base. Aerobic oxidation of alcohols catalyzed by PI-Au was strongly influenced by addition of a base. Although oxidation of amines was seldom affected by external addition of a base, a substrate itself that was a secondary amine might work as a base in the amine oxidation. It is possible that the tertiary amine in the polymer, which is more basic than the substrate, can play a role as a base and enhance the reactivity more effectively, cooperating with gold nanoclusters inside the same reaction environment of the polymer.

Another effect of the tertiary amine can be explained by controlling the balance of adsorption and desorption. The product, an imine, can be adsorbed strongly on gold nanoclusters; thus, a higher temperature is required to replace it on a substrate for amine oxidation than for alcohol oxidation. The tertiary amine in the polymer can eliminate an adsorbed imine and make the catalytic cycle faster because of its nucleophilicity and bulkiness (Figure 10).

Substrate Scope. The scope of the substrates was examined using PI-Au catalysts. First, benzylaniline derivatives were chosen as substrates (Table 6). The reactions proceeded smoothly at 100 °C with electron-donating groups on the benzene ring of the benzyl group both by PI-Au **2c** and **7**, however a higher temperature was required when electron-withdrawing groups existed on the benzene ring of the benzyl group. On the other hand, electron-withdrawing groups on the benzene ring connected to nitrogen did not affect the reactivity. These results suggest that hydride transfer at the benzylic position may be a rate-determining step similar to oxidation of alcohols to carbonyl compounds.[11]

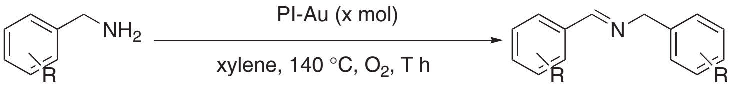
Table 6. Substrate Scope of Oxidation of Benzylaniline Derivatives



Entry	PI-Au	R^1, R^2	Conditions	Product	Yield/%[a)]
1	**7**	4-MeO, 4-Cl	Toluene, 100 °C, 12 h	**15**	89
2	**7**	4-MeO, 4-Br	Toluene, 100 °C, 12 h	**16**	69
3	**7**	4-Cl, H	Toluene, 100 °C, 12 h	**17**	6
4	**7**	4-Cl, H	Xylene, 140 °C, 20 h	**17**	91
5	**7**	4-Br, H	Toluene, 100 °C, 12 h	**18**	15
6	**7**	4-Br, H	Xylene, 140 °C, 20 h	**18**	>99
7	**7**	4-MeO, H	Toluene, 100 °C, 20 h	**19**	>99
8	**7**	3,4-diMeO, H	Toluene, 100 °C, 20 h	**20**	92
9	**2c**	2,4-diMeO, H	Toluene, 100 °C, 24 h	**21**	82[b)]
10	**2c**	2,4-diMeO, H	Xylene, 140 °C, 24 h	**21**	94[b)]
11	**7**	3,4,5-triMeO, H	Toluene, 100 °C, 20 h	**22**	60[b)]
12	**2c**	H, H	Xylene, 140 °C, 24 h	**23**	90[b)]

a) Isolated yield. b) Determined by GC analysis.

Table 7. Substrate Scope of Oxidation of Primary Benzylamines



R	PI-Au	x/mol %	T/h	Product	Yield/%[a)]
H	**2a**	4	24	**14**	70[b)]
H	**7**	2.5	30	**14**	90[b)]
p-MeO	**2a**	1	24	**24**	72[b)]
p-MeO	**2b**	1	24	**24**	70[b)]
p-MeO	**2c**	1	24	**24**	88[b)]
p-MeO	**7**	1	24	**24**	99[b)]
o-MeO	**2a**	1	24	**25**	61
m-MeO	**2a**	1	24	**26**	52
p-CF_3	**2a**	4	24	**27**	45

a) Isolated yield. b) Determined by GC analysis.

Next, oxidation of primary benzylamines was examined (Table 7). A high temperature was required to obtain the desired imine in high yields, and electron-donating groups on the benzene ring facilitated the reaction, similar to the case of benzylaniline substrates, probably for the same reasons.

Oxidative aromatization reactions also proceeded well in the presence of PI-Au catalysts (Table 8). Indoline and tetrahydroquinoline were oxidized to indole and quinoline respectively however dihydroquinoline was not observed. On the other hand, tetrahydroisoquinoline was oxidized to dihydroisoquinoline as a major product, isoquinoline being a minor product. The best result was obtained at 100 °C in the presence of PI-Au **7**, and total yield decreased at higher temperatures, probably because of decomposition of the products.

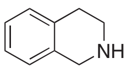
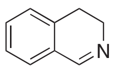
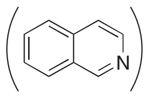
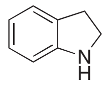
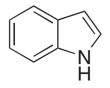
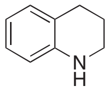
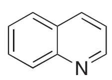
N-Phenyltetrahydroisoquinoline was oxidized to a mixture of amide **8** and further oxidized amide **9** in the presence of PI-Au **7** (Table 9). While the ratio of amide **9** was increased at higher temperature, the total yield was decreased.

Recovery and Reuse of PI-Au. PI-Au **7** could be recovered and reused without loss of activity at least seven times by simple filtration and drying (Table 10). We chose *p*-methoxybenzylaniline as model substrate for recovery and reuse because analytically pure product could be obtained after filtration of catalyst and concentration. PI-Au **7** was added to a solution of *p*-methoxybenzylaniline in toluene. The mixture was stirred at 100 °C under oxygen atmosphere (with oxygen balloon) for 20 h. After filtration of the catalyst, solvent was removed to afford analytically pure **19**. Filtered PI-Au was dried in vacuo and collected. A small amount of catalyst could not be recovered because it was trapped by filtration paper. Recovered PI-Au was used for the second reaction and reaction scale was adjusted depending on the amount of recovered catalyst.

Substrate Scope of One-Pot Deprotection of the *p*-Methoxybenzyl Group Catalyzed by PI-Au. One-pot oxidative deprotection of the *p*-methoxybenzyl group of a secondary amine was examined (Table 11), and both aryl and alkyl amines could be obtained in high yields. Substrates **11a** and **12a** had two α-hydrogens of amine, which could be oxidized, however, only benzylideneamines formed and gave aliphatic amines after hydrolysis. On the other hand, a tertiary amine substrate did not react in xylene at 140 °C (Scheme 5).

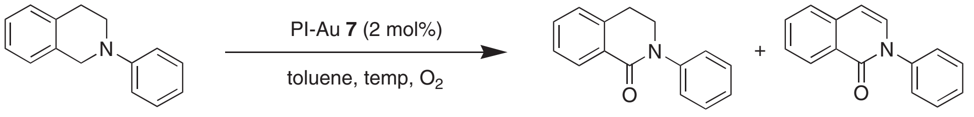
Table 8. Substrate Scope of the Aromatization Reaction

$$\text{amine} \xrightarrow[\text{conditions, O}_2]{\text{PI-Au (2 mol\%)}} \text{imine}$$

Amine	Product	PI-Au (2 mol %)	Conditions	Yield[a]/%
		7	Xylene, 140 °C, 24 h	79 (11)[b]
		7	Toluene, 120 °C, 24 h	82 (12)[b]
		7	Toluene, 100 °C, 24 h	87 (13)[b]
		2a	Xylene, 140 °C, 24 h	64
		2b	Xylene, 140 °C, 24 h	75
		2c	Xylene, 140 °C, 24 h	57
		7	Xylene, 140 °C, 24 h	76

a) Determined by GC analysis. b) Isolated as a mixture and ratio was determined by ^{1}H NMR.

Table 9. Oxidation of Tetrahydroisoquinoline Derivative



8 9

Entry	Temperature/°C	Time/h	**8**/**9** yield/%[a]
1	120	20	29/48
2	100	20	46/35

a) Isolated as a mixture and ratio was determined by ^{1}H NMR.

Therefore, the tertiary amine group in the polymer might be intact under these oxidative conditions.

Conclusion

Polymer-incarcerated gold (PI-Au) catalysts were applied to aerobic oxidation of amines to imines. Investigation of recovery and reuse of PI-Au in the amine oxidation, careful TEM and STEM analysis to examine distribution and average size of clusters and modified preparation methods of the catalysts to control cluster size revealed interesting relationship among Au loading, cluster size, and reactivity. Relatively large Au clusters (5 to 10 nm) seem to be more effective for amine oxidation than small Au clusters (2 to 3 nm), which, in contrast, showed excellent reactivity for aerobic oxidation of alcohols. Catalysts prepared from a polymer with a tertiary amine group showed excellent catalytic activity, probably because of the cooperative effect of such functional groups with Au clusters.

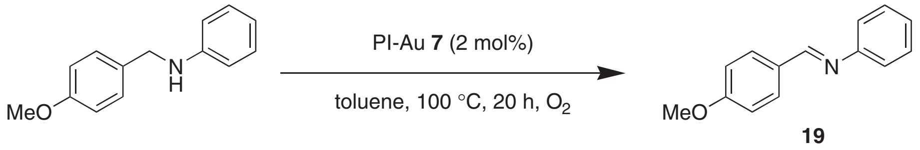
Various primary and secondary benzylamines could be successfully oxidized to the corresponding imines using this oxidation system. Aromatization reactions and one-pot deprotection of *p*-methoxybenzyl groups could be achieved. Moreover, the catalyst could be reused several times by simple operations without significant loss of activity.

Further investigations to reveal the reaction mechanism and relationship between reactivity and cluster size would provide valuable information about Au cluster catalysis.

Experimental

General. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or JNM-LA600 spectrometer. Tetramethylsilane ($\delta = 0$) was used as an internal standard for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. The structures of the known compounds were confirmed by comparison with commercially available compounds or data shown in the literature. GC analysis was performed on a Shimadzu GC-2010 apparatus (column: J & W SCIENTIFIC DB-1; gas pressure: 157.5 kPa, total flow: 41.3 mL min^{-1}, column flow: 0.93 mL min^{-1}, linear velocity: 21.1 cm s^{-1}, split ratio: 40:1, injection temperature: 300 °C, detector temperature: 300 °C). Inductively coupled plasma (ICP) analysis was performed on Shimadzu ICPS-7510 equipment. High-resolution electrospray ionization mass spectra (HR-MS) were measured with JEOL JMS-T100TD AccuTOF TLC. Water was treated by MILLIPORE Elix-UV before use. Column chromatography was performed on silica gel 60 (Merck), and preparative TLC was carried out using Wakogel B-5F (Wako Pure Chemical

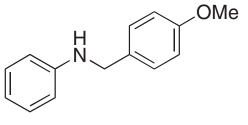
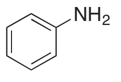
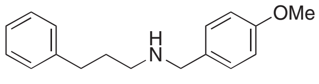
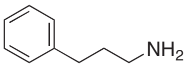
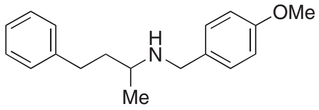
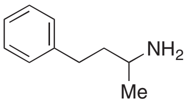
Table 10. Recovery and Reuse of PI-Au **7**



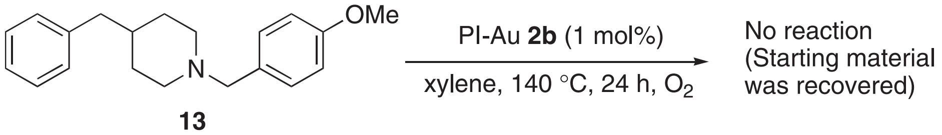
Run	1st	2nd	3rd	4th	5th	6th	7th
Yield/%[a)]	>99	>99	>99	>99	>99	>99	>99

a) Isolated yield.

Table 11. Substrate Scope of Oxidative Deprotection of PMB Groups

Entry	Substrate	Product	Conditions	Yield /%[a)]
1	 **10a**	 **10b**	Xylene, 140 °C	91
2	 **11a**	 **11b**	Toluene, 100 °C	92
3	 **12a**	 **12b**	Toluene, 100 °C	88

a) Isolated yield.



Scheme 5. Oxidative deprotection of PMB at a tertiary amine.

Industry). STEM and TEM images were obtained using a JEOL JEM-2100F instrument operated at 200 kV and JEOL JEM-1010 instrument operated at 80 kV. All TEM specimens were prepared by placing a drop of solution on carbon-coated Cu grids and allowing to dry in air (without staining).

Preparation of ΔPI-Au 3. PI-Au **2** (55 mg), prepared by a previously reported method,[9a] was heated in xylene (2 mL) at 140 °C under Ar atmosphere for 0.5, 1, 3, 8, and 24 h. The mixture was cooled to room temperature and the catalyst was collected by filtration and washed with EtOAc (5 mL). The catalyst was dried in vacuo to afford ΔPI-Au **3**.

Preparation of 1-(4-Vinylbenzyl)piperidine.[12] K_2CO_3 (16.14 g) was added to a solution of 4-vinylbenzyl chloride (9.26 g) and piperidine (5.13 g) in acetonitrile (50 mL). The mixture was refluxed for 2 h and cooled to room temperature. Solvent was removed and the residue was purified by column chromatography to afford 1-(4-vinylbenzyl)piperidine (10.7 g, 87%). ^{1}H NMR ($CDCl_3$): δ 1.38–1.40 (m, 2H), 1.49–1.56 (m, 4H), 3.42 (s, 2H), 5.17 (d, 1H, $J = 10.6$ Hz), 5.68 (d, 1H, $J = 17.4$ Hz), 6.66 (dd, 1H, $J = 10.9$ Hz, 17.4 Hz), 7.21–7.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 24.4, 26.0, 54.5, 63.6, 113.3, 125.9, 129.4, 136.2, 136.7, 138.3.

Preparation of Copolymer 6. Styrene (1.07 g), glycidyl 4-vinylbenzyl ether (1.90 g), 2-(2-{2-[2-(4-vinylbenzyloxy)ethoxy]ethoxy}ethoxy)ethanol (3.15 g), 1-(4-vinylbenzyl)piperidine (342 mg), and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (102.5 mg) were combined in chloroform (11.0 mL). The mixture was stirred for 72 h at room temperature. The resulting polymer solution was diluted with THF (15 mL) and slowly poured into diethyl ether (800 mL). The solvent was removed by decantation and the residue was dissolved again in THF (15 mL). The polymer solution was slowly poured into diethyl ether (800 mL) again. The same procedure was repeated a total of three times. The precipitated polymer was filtered and washed with ether several times and dried in vacuo within 10 min to afford the desired copolymer (**6**, 3.75 g). If the polymer was dried in vacuo for too long time, crosslinking sometimes occurred, therefore, polymer was dissolved in THF (37.5 mL) and stored in refrigerator. The mole ratio of the components was determined by ^{1}H NMR analysis.

Preparation of PI-Au 4. Copolymer **1** (420.6 mg)[9a] and $NaBH_4$ (27.0 mg) were dissolved in diglyme (25 mL) at room temperature. Chlorotriphenylphosphine gold(I) (150.0 mg) with 3 mL of THF was slowly added to this solution, whereupon the solution turned wine red. The mixture was stirred for 3 h at room temperature and diethyl ether (80 mL) was slowly added to the mixture at room temperature. Brown coacervates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethyl ether several times and dried at room temperature. Next, the catalyst capsules were heated at 150 °C in mesitylene (20 mL) for 5 h. The prepared catalyst was washed with water, dichloromethane (DCM), and THF, crushed and dried to afford a wine-red powder. This powder was heated at 150 °C for 5 h without solvent to afford PI-Au **4** (283.5 mg). 10–20 mg of PI-Au **4** was heated in a mixture of sulfuric acid and nitric acid at 200 °C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the loading of gold (0.805 mmol g^{-1} Au).

Preparation of PI-Au 7. Copolymer **6** (344.2 mg) and $NaBH_4$ (27.0 mg) were dissolved in diglyme (25 mL) at room temperature. Chlorotriphenylphosphine gold(I) (150.0 mg) with 3 mL of THF was slowly added to this solution, whereupon the solution turned wine red. The mixture was stirred for 3 h at room temperature and diethyl ether (80 mL) was slowly added to the mixture at room temperature. Brown coacervates enveloped the metal dispersed in the medium. The catalyst capsules were then washed with diethyl ether several times and dried at room temperature. Next, the catalyst capsules were heated at 150 °C in mesitylene (20 mL) for 5 h. The prepared catalyst was washed with water, DCM, and THF, crushed and dried to afford a wine-red powder. This powder was heated at 150 °C for 5 h without solvent to afford PI-Au **7** (279.6 mg). 10–20 mg of PI-Au **7** was heated in a mixture of sulfuric acid and nitric acid at 200 °C for 3 h, the mixture was cooled to room temperature and aqua regia was added. The amount of gold in the resulting solution was measured by ICP analysis to determine the loading of gold (0.887 mmol g^{-1} Au).

A Typical Procedure for Oxidation of Dibenzylamine Catalyzed by PI-Au (Determination of Yield by GC Analysis, Table 5, PI-Au 7, 100 °C, 12 h). PI-Au **7** (2 mol % Au, 10.3 mg) was added to a solution of dibenzylamine (50.3 mg, 0.255 mmol) in toluene (1 mL). The mixture was stirred at 100 °C under oxygen atmosphere (with oxygen balloon) for 12 h. After filtration of the catalyst, anisole was added as an internal standard. The mixture was analyzed by GC and yield was calculated as *N*-(benzylidene)benzylamine: 44.0 mg, 88%; dibenzylamine: 3.6 mg, 7%; benzaldehyde: 1.3 mg, 5%. After determining the yield, the solvents of the mixture were removed in vacuo. To each residue were added sulfuric acid and aqua regia then the volume of the residue was adjusted to 50 mL using water to give a sample for ICP analyses for the measurement of the leaching of gold (Au was not detected; <0.04%).

A Typical Procedure for Oxidation of Amine Catalyzed by PI-Au (Isolation by Filtration) and the Following Recovery and Reuse of PI-Au. PI-Au **7** (2 mol % Au, 53.8 mg) was added to a solution of *N*-(*p*-methoxybenzyl)aniline (245.0 mg, 0.364 mmol) in toluene (1 mL). The mixture was stirred at 100 °C under oxygen atmosphere (with oxygen balloon) for 20 h. After filtration of the catalyst, solvent was removed to afford analytically pure **19** (244.0 mg, >99% yield). Filtered PI-Au was dried in vacuo and collected (50.4 mg). A small amount of catalyst could not be recovered because it was trapped by filtration paper. Recovered PI-Au was used for the second reaction and reaction scale was adjusted depending on the amount of recovered catalyst.

Oxidation of 1,2,3,4-Tetrahydro-2-phenylisoquinoline Catalyzed by PI-Au (Isolation by pTLC). PI-Au **7** (2 mol % Au, 10.6 mg) was added to a solution of 1,2,3,4-tetrahydro-2-phenylisoquinoline (43.8 mg, 0.210 mmol) in toluene. (1 mL) The mixture was stirred at 120 °C under oxygen atmosphere (with oxygen balloon) for 20 h. After filtration of the catalyst, solvent was removed. The mixture was separated by preparative TLC (ethyl acetate:hexane = 3:1). Yellow oil was obtained in 35.7 mg and was analyzed by ^{1}H NMR to determine the ratio of 3,4-dihydro-2-phenylisoquinolin-1(2*H*)-one (29% yield) and 2-phenylisoquinolin-1(2*H*)-one (48% yield).

Oxidation of 1,2,3,4-Tetrahydroisoquinoline Catalyzed by PI-Au (Isolation by pTLC). PI-Au **7** (2 mol % Au, 10.6 mg) was added to a solution of 1,2,3,4-tetrahydroisoquinoline (35.4 mg, 0.266 mmol) in xylene (1 mL). The mixture was stirred at 140 °C under oxygen atmosphere (with oxygen balloon) for 24 h. After filtration of the catalyst, solvent was removed. The mixture was separated by preparative TLC (ethyl acetate:hexane = 3:1). Yellow oil was obtained in 31.4 mg and was analyzed by ^{1}H NMR to determine the ratio of 3,4-dihydroisoquinoline (79% yield) and isoquinoline (11% yield).

***N*-(Benzylidene)benzylamine (14):**[13] ^{1}H NMR ($CDCl_3$): δ 4.82 (s, 2H), 7.24–7.28 (m, 1H), 7.33–7.43 (m, 4H), 7.41–7.43 (m, 3H), 7.77–7.80 (m, 2H), 8.40 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 65.0, 127.0, 127.9, 128.2, 128.5, 128.6, 130.7, 136.1, 139.3, 161.9.

***N*-(4-Methoxybenzylidene)-4-chloroaniline (15):**[14] ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H), 6.90 (d, 2H, $J = 8.2$ Hz), 7.03–7.05 (m, 2H), 7.24–7.26 (m, 2H), 7.75 (d, 2H, $J = 7.6$ Hz), 8.26 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.4, 114.2, 122.2, 129.0, 129.2, 130.6, 131.0, 150.9, 160.0, 162.4.

***N*-(4-Methoxybenzylidene)-4-bromoaniline (16):**[14] ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H), 6.96 (d, 2H, $J = 8.9$ Hz), 7.05 (d, 2H, $J = 8.9$ Hz), 7.47 (d, 2H, $J = 8.3$ Hz), 7.81 (d, 2H, $J = 8.3$ Hz), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.4, 114.3, 118.8, 122.6, 129.0, 130.6, 132.1, 151.3, 160.0, 162.5.

***N*-(4-Chlorobenzylidene)aniline (17):**[13] ^{1}H NMR ($CDCl_3$): δ 7.22–7.28 (m, 3H), 7.40–7.48 (m, 4H), 7.84–7.87 (m, 2H), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 120.8, 126.2, 129.0, 129.2, 129.9, 134.7, 137.3, 151.6, 158.8.

***N*-(4-Bromobenzylidene)aniline (18):**[15] ^{1}H NMR ($CDCl_3$): δ 7.22–7.28 (m, 3H), 7.40–7.44 (m, 2H), 7.63 (d, 2H, $J = 8.2$ Hz), 7.8 (d, 2H, $J = 8.2$ Hz), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 120.8, 125.9, 126.2, 129.2, 130.1, 132.0, 135.6, 151.7, 158.9.

***N*-(4-Methoxybenzylidene)aniline (19):**[13] ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H), 7.01 (d, 2H, $J = 8.2$ Hz), 7.22–7.27 (m, 3H), 7.40–7.53 (m, 2H), 7.88 (d, 2H, $J = 8.9$ Hz), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.2, 114.1, 114.9, 120.8, 125.4, 129.0, 130.4, 152.2, 159.5, 162.1.

N-(3,4-Dimethoxybenzylidene)aniline (20):[16] ^{1}H NMR ($CDCl_3$): δ 3.94 (s, 3H), 3.99 (s, 3H), 6.93 (d, 1H, $J = 8.2$ Hz), 7.22–7.26 (m, 3H), 7.30–7.34 (m, 1H), 7.39–7.43 (m, 2H), 7.65 (d, 1H, $J = 1.8$ Hz), 8.37 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.8, 56.0, 108.9, 110.4, 120.7, 124.3, 125.4, 129.0, 129.4, 149.3, 151.9, 152.1, 159.7.

N-(4-Methoxybenzylidene)-4-methoxybenzylamine (24):[13] ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H), 3.84 (s, 3H), 4.73 (s, 2H) 6.87–6.93 (m, 4H), 7.25–7.26 (m, 2H), 7.71–7.73 (m, 2H), 8.29 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.2, 55.3, 64.3, 113.8, 113.9, 129.1, 129.7, 131.6, 158.6, 160.8, 161.6.

N-(2-Methoxybenzylidene)-2-methoxybenzylamine (25):[13] ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 3H), 3.86 (s, 3H), 4.82 (s, 2H), 6.85–6.96 (m, 4H), 7.20–7.39 (m, 3H), 8.00–8.03 (m, 1H), 8.83 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.3, 55.5, 59.6, 110.2, 110.9, 120.5, 120.7, 124.9, 127.5, 127.9, 128.2, 129.1, 131.7, 157.1, 158.3, 158.8.

N-(3-Methoxybenzylidene)-3-methoxybenzylamine (26):[13] ^{1}H NMR ($CDCl_3$): δ 3.78 (s, 3H), 3.82 (s, 3H), 4.78 (s, 2H), 6.78–6.97 (m, 4H), 7.22–7.37 (m, 4H), 8.33 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.2, 55.4, 64.9, 111.7, 112.4, 113.6, 117.6, 120.3, 121.6, 129.46, 129.54, 137.6, 140.8, 159.8, 159.9, 162.0.

N-(4-Trifluoromethylbenzylidene)-4-trifluoromethylbenzylamine (27):[13] ^{1}H NMR ($CDCl_3$): δ 4.88 (s, 2H), 7.44–7.47 (m, 2H), 7.58–7.69 (m, 4H), 7.87–7.90 (m, 2H), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 64.3, 120.0 (d, $J = 34.3$ Hz), 122.7 (d, $J = 34.3$ Hz), 125.4 (q, $J = 3.8$ Hz), 125.6 (q, $J = 3.8$ Hz), 128.1, 128.5, 129.4 (q, $J = 32.4$ Hz), 132.5 (q, $J = 32.4$ Hz), 139.0 (d, $J = 1.9$ Hz), 143.1, 161.1.

A Typical Procedure for Preparation of N-(4-Methoxybenzylidene)aniline (19) (GC Standard). Aniline (1.0 g) and anisaldehyde (1.5 g) were dissolved together in ethanol and left to stand overnight at room temperature. The solvent was evaporated off, and the product was recrystallized from EtOH to give *N*-(4-methoxybenzylidene)aniline (**19**) (1.92 g, 85%).

Preparation of 24 (GC Standard). *p*-Methoxybenzaldehyde was added to a solution of *p*-methoxybenzylamine in CH_2Cl_2. The mixture was stirred at room temperature for 20 h with molecular sieves 3A. The mixture was filtered through a celite pad and concentrated. The resulting crude oil was purified by distillation under reduced pressure (178 °C, <1 mmHg) to give **24** as a colorless oil.

N-(2,4-Dimethoxybenzylidene)aniline (21):[16] ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 6H), 6.46 (d, 1H, $J = 2.76$ Hz), 6.59 (t, 1H, $J = 2.10$ Hz), 7.17–7.21 (m, 3H), 7.34–7.37 (m, 2H), 8.12 (br, 1H), 8.80 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.2, 55.3, 97.8, 105.6, 118.0, 120.9, 125.1, 128.7, 128.8, 152.9, 155.7, 160.8, 163.6.

N-(3,4,5-Trimethoxybenzylidene)aniline (22):[17] ^{1}H NMR ($CDCl_3$): δ 3.92–3.96 (m, 9H), 7.13–7.26 (m, 5H), 7.40 (t, 2H, $J = 7.56$ Hz), 8.36 (s, 1H).

N-(Benzylidene)aniline (23):[13] ^{1}H NMR ($CDCl_3$): δ 7.22–7.25 (m, 3H), 7.37–7.41 (m, 2H), 7.43–7.46 (m, 3H), 7.90–7.92 (m, 2H), 8.43 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 120.7, 125.8, 128.6, 128.7, 129.0, 131.2, 136.1, 151.9, 160.1.

A Typical Procedure for Preparation of N-Benzylaniline. $NaBH_4$ was added to a solution of *N*-(4-methoxybenzylidene)aniline (1.0 g, 4.73 mmol) in MeOH at room temperature. The mixture was stirred at the same temperature for 12 h. The reaction was worked up with water and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and solvent was removed in vacuo. The residue was purified by column chromatography (hexane:ethyl acetate = 15:1) as an eluant to give *N*-(4-methoxybenzyl)aniline (0.9547 g, 96%).

N-(4-Methoxybenzyl)aniline (Table 6, Entry 7): ^{1}H NMR ($CDCl_3$): δ 3.80 (s, 3H), 4.08 (br, 1H), 4.24 (s, 2H), 6.64 (d, 2H, $J = 7.56$ Hz), 6.72 (t, 1H, $J = 6.90$ Hz), 6.88 (t, 2H, $J = 2.10$ Hz), 7.15–7.19 (m, 2H), 7.29 (d, 2H, $J = 8.88$ Hz).

N-(4-Chlorobenzyl)aniline (Table 6, Entries 3 and 4): ^{1}H NMR ($CDCl_3$): δ 4.26 (br, 1H), 4.43 (s, 2H), 6.61 (d, 2H, $J = 7.56$ Hz), 6.71 (t, 1H, $J = 7.56$ Hz), 7.15–7.21 (m, 4H), 7.24–7.42 (m, 2H).

N-(3,4,5-Trimethoxybenzyl)aniline (Table 6, Entry 11): ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 9H), 4.26 (s, 2H), 6.61 (s, 2H), 6.67 (d, 2H, $J = 7.56$ Hz), 6.75 (t, 2H, $J = 6.84$ Hz), 7.19 (t, 2H, $J = 8.22$).

N-(2,4-Dimethoxybenzyl)aniline (Table 6, Entries 9 and 10): ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H), 3.82 (s, 3H), 4.24 (s, 2H), 6.42 (dd, 1H, $J = 2.70$, 8.22 Hz), 6.47 (d, 1H, $J = 2.4$ Hz), 6.65–6.70 (m, 3H), 7.14–7.25 (m, 3H).

A Typical Procedure for Preparation of an N-(4-Methoxybenzyl)amine. 4-Methoxybenzylamine (1.6 g, 11.3 mmol) was added to a cooled solution of 3-phenyl-1-bromopropane (1.5 g, 7.53 mmol) in CH_2Cl_2 (25 mL). Et_3N (2.1 mL, 15.1 mmol) was added to the mixture under ice cooling. This was stirred at room temperature for 3 h. Water was added to work up the reaction and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2. Et_3N (2.0 equiv) and Boc_2O (1.5 equiv) were added to the mixture. This was stirred at room temperature for 12 h. Water was added to the mixture to work up the reaction and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine and concentrated in vacuo. The residue was purified by silica gel column chromatography to give a pale red-orange oil (0.9447 g, 35%). This oil was then dissolved in dioxane. 4 M HCl/dioxane was added to the solution. The solution was stirred at room temperature for 12 h. The solvent was removed in vacuo. The resulting solid was triturated with isopropyl ether/isopropyl alcohol to give colorless crystals. These were suspended in ethyl acetate and washed with 1 M NaOH. The organic layer was dried over Na_2SO_4 and concentrated to give *N*-(4-methoxybenzyl)-3-phenylpropan-1-amine (**11a**) (0.62 g, 32% three steps).

N-(4-Methoxybenzyl)-3-phenylpropan-1-amine (11a): ^{1}H NMR ($CDCl_3$): δ 1.65 (br, 1H), 1.83 (quintet, 2H, $J = 7.50$ Hz), 2.64–2.67 (m, 4H), 3.71 (s, 2H), 3.80 (s, 3H), 6.86 (dd, 2H, $J = 2.10$, 4.08 Hz), 7.16–7.28 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 31.7, 33.6, 48.8, 53.4, 55.3, 113.8, 125.7, 128.3, 128.4, 129.3, 132.5, 142.2, 158.6.

N-(4-Methoxybenzyl)-4-phenylbutan-2-amine (12a): ^{1}H NMR ($CDCl_3$): δ 1.13 (d, 3H, $J = 6.18$ Hz), 1.23 (br, 1H), 1.63–1.68 (m, 1H), 1.78–1.81 (m, 1H), 2.62–2.67 (m, 2H), 2.70–2.74 (m, 1H), 3.67 (d, 2H, $J = 12.36$ Hz), 3.76 (d, 2H, $J = 12.36$ Hz), 3.80 (s, 3H), 6.85 (dd, 2H, $J = 2.04$, 6.18 Hz), 7.17–7.28 (m, 7H). ^{13}C NMR ($CDCl_3$): δ 31.7, 33.6, 48.8, 53.4, 55.3, 113.8, 125.7, 128.3, 128.4, 129.3, 132.5, 142.2, 158.6.

A Typical Procedure for Oxidative Deprotection of 4-Methoxybenzylamine. PI-Au **2b** (15.6 mg, 0.25 mmol g^{-1})

was added to a solution of *N*-(4-methoxybenzyl)-3-phenylpropan-1-amine (**11a**) (99.3 mg, 0.389 mmol) in toluene (2 mL). The mixture was stirred at 100 °C for 24 h under oxygen atmosphere. The catalyst was removed by filtration and washed with ethyl acetate. A mixture of MeOH (2 mL) and 1 M HCl(aq) (1 mL) was added to the filtrate and stirred for 12 h. The aqueous phase was washed with ethyl acetate and NaOH(aq) was added to basify the solution (pH 12–13). The mixture was extracted with ethyl acetate and the combined organic layer was dried over Na_2SO_4. Solvent was removed in vacuo and the residue was purified by column chromatography to give 3-phenylpropan-1-amine (**11b**) (48.3 mg, 92%).

3-Phenylpropan-1-amine (11b): ^1H NMR ($CDCl_3$): δ 1.25 (br, 2H), 1.77 (quintet, 2H, $J = 6.90$ Hz), 2.65 (t, 2H, $J = 7.56$ Hz), 2.73 (t, 2H, $J = 6.90$ Hz), 7.17–7.20 (m, 3H), 7.25–7.29 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 33.3, 35.4, 41.8, 125.8, 128.3, 128.4, 142.1.

4-Phenylbutan-2-amine (12b): ^1H NMR ($CDCl_3$): δ 1.11 (d, 3H, $J = 6.18$ Hz), 1.65–1.68 (m, 2H), 2.09 (br, 2H), 2.62–2.93 (m, 2H), 2.92 (q, 1H, $J = 6.90$ Hz), 7.15–7.29 (m, 3H), 7.25–7.28 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 23.7, 32.8, 41.5, 46.6, 125.5, 128.3, 128.3, 142.2.

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