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Pt–Sn/γ-Al_2O_3-Catalyzed Highly Efficient Direct Synthesis of Secondary and Tertiary Amines and Imines

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Abstract: Versatile syntheses of secondary and tertiary amines by highly efficient direct N-alkylation of primary and secondary amines with alcohols or by deaminative self-coupling of primary amines have been successfully realized by means of a heterogeneous bimetallic Pt–Sn/γ-Al_2O_3 catalyst (0.5 wt% Pt, Pt/Sn molar ratio = 1:3) through a borrowing-hydrogen strategy. In the presence of oxygen, imines were also efficiently prepared from the tandem reactions of amines with alcohols or between two primary amines. The proposed mechanism reveals that an alcohol or amine substrate is initially dehydrogenated to an aldehyde/ketone or NH-imine with concomitant formation of a [PtSn] hydride. Condensation of the aldehyde/ketone species or deamination of the NH-imine intermediate with another molecule of amine forms an N-substituted imine which is then reduced to a new amine product by the in-situ generated [PtSn] hydride under a nitrogen atmosphere or remains unchanged as the final product under an oxygen atmosphere. The Pt–Sn/γ-Al_2O_3 catalyst can be easily recycled without Pt metal leaching and has exhibited very high catalytic activity toward a wide range of amine and alcohol substrates, which suggests potential for application in the direct production of secondary and tertiary amines and N-substituted imines.

Keywords: alcohols · alkylation · amines · borrowing hydrogen · imines

Introduction

Amines[1] and imines[2] are important intermediates that have been extensively applied in organic synthesis and the chemical industry. The reaction between amines and organic halides has been the major method utilized to prepare secondary and tertiary amines but this method is often associated with environmental problems, uses expensive starting materials, and exhibits low selectivity for the desired products. Reductive amination of aldehydes or ketones with amines by means of high-pressure hydrogenation is another known route to higher-order amines. Imines are often synthesized by acid-promoted condensation of carbonyl compounds with primary amines,[3] oxidation of secondary amines,[4] or by other methods.[5] Recently, transition-metal-catalyzed direct N-alkylation of amines[6–8] and ammonia[9] with alcohols has been reported as an alternative route to amines through a borrowing-hydrogen (BH) strategy. Through a BH process, amines,[6–9] imines,[10] and amides[11] can be formed by variation of the transition-metal-complex catalyst and reaction conditions. Deaminative N-alkylation between two amines was also documented for the preparation of secondary and tertiary amines.[12] However, examples of the BH strategy in amine/imine synthesis with supported catalysts are only scattered.[10e,13] In a BH process, imines are usually formed as the intermediates, and can be further reduced to amine products by the hydrogen species generated in-situ, or occasionally isolated as the major products.[10] In principle, catalysts suitable for a BH process should be:

1) highly active for dehydrogenation of an alcohol or amine substrate into an aldehyde/ketone or NH-imine species.
2) effective to promote condensation of the in-situ generated aldehyde/ketone species with an amine to form an N-substituted imine intermediate, or effective for deaminative coupling of the in-situ generated NH-imine with a primary amine substrate.
3) highly active for reduction of the resultant N-substituted imine intermediate to form a new amine product.
4) readily available and recyclable, in view of industrial application.

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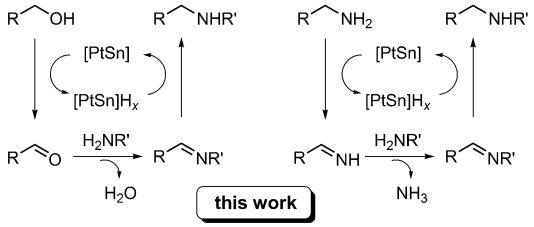
During the search for a readily available, applicable, and highly active catalyst for a BH process, we found that heterogeneous bimetallic Pt–Sn/γ-Al_2O_3 catalysts meet these requirements. Pt–Sn/γ-Al_2O_3 catalysts have usually been applied to alkane dehydrogenation,[14] reforming processes,[15] and hydrogenation[16] in the petroleum industry. Moreover, Pt nanoparticles on TiO_2 can mediate photoirradiation of *o*-arylenediamines in alcohol to form benzimidazoles.[8e] In the gas phase at 200–290 °C, primary amines can interact with methanol over γ-Al_2O_3 to yield a mixture of amines.[17] Herein, we report the first versatile synthesis of amines and imines from the direct N-alkylation of amines with alcohols or amines by means of a heterogeneous bimetallic Pt–Sn/γ-Al_2O_3 catalyst (Scheme 1).



Scheme 1. Pt–Sn/γ-Al_2O_3-catalyzed direct N-alkylation of amines with alcohols and amines through a BH strategy.

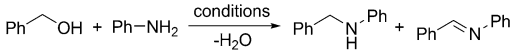
Results and Discussion

Catalyst preparation: The Pt–Sn/γ-Al_2O_3 catalyst has been revealed as a useful heterogeneous bimetallic catalyst for the dehydrogenation of long-chain paraffins and was prepared by our previously reported method;[14] monometallic Pt/γ-Al_2O_3 and bimetallic Pt–Sn/TiO_2 catalysts were made in a similar fashion. The platinum content was fixed at 0.5 wt % in all of the heterogeneous catalysts and the tin content was varied (Table 1). Prior to use, these heterogeneous catalysts were reduced in a hydrogen flow at 400 °C for 2 h, cooled to room temperature under a H_2 atmosphere, and then kept for use in a desiccator under an air atmosphere. It has been known that PtSn alloy, SnO_x ($x=1$, 2), and γ-Al_2O_3 phases coexist in a Pt–Sn/γ-Al_2O_3 catalyst.[14–16,18] In this bimetallic catalyst, tin acts as a spacer to disperse the platinum particles over the Al_2O_3 support surface, which enhances the activity and stability of the catalyst remarkably.[19] In addition, the presence of tin in the bimetallic Pt–Sn/γ-Al_2O_3 catalyst modifies the electronic state of the supported Pt particles by electron transfer from tin to platinum. This results in reduction of the binding energy of the intermediate species and products thus, suppresses further reactions of some chemical bonds.[16c] The γ-Al_2O_3 support usually shows Lewis acidity, highly desired in our case, to facilitate condensation of the aldehyde/ketone intermediates with amines to generate imines.

Screening of conditions for direct *N*-benzylation of aniline (2a) with benzyl alcohol (1a): In our initial studies, a heterogeneous Pt/γ-Al_2O_3 catalyst that contained 0.5 wt % Pt was tested in the *N*-benzylation of aniline (**2a**) with benzyl alcohol (**1a**). In a sealed reactor under nitrogen atmosphere, the reaction was heated at reflux in *o*-xylene for 24 h and afforded *N*-phenylbenzylamine (**3aa**, 14 %) and imine **4a** (19 %) (Table 1, entry 1). Incorporating a second metal, specifically, tin, improved the catalyst activity remarkably; amine **3aa** was obtained in 80 % yield within 8 h by using a bimetallic Pt–Sn/γ-Al_2O_3 catalyst (catalyst **I**, Pt/Sn = 1:1, Table 1, entry 2). Increasing the Pt/Sn molar ratio from 1:1 to 1:9 further improved the yield of **3aa** (91–97 %, Table 1, entries 3–7). The best result was obtained with catalyst **III** (Pt/Sn = 1:3); the reaction formed **3aa** in 95 % isolated yield (Table 1, entry 4). The high tin content in catalysts **IV**–**VI** (Pt/Sn = 1:5–1:9) may partially block exposure of the Pt^0 metal surface required for the BH process, which leads to lower reaction efficiency (Table 1, entries 5–7). Use of excessive alcohol (1.1 equiv) was not necessary (Table 1, entry 10), and the reaction proceeded less efficiently either with an atmospheric nitrogen balloon or at a lower temperature (110 °C) (Table 1, entries 11 and 12). An air atmosphere favored formation of imine **4a** (46 %) as the major product (Table 1, entry 13). The Pt–Sn/TiO_2 catalyst only exhibited a moderate catalytic activity, clearly suggestive of a support effect[20] (Table 1, entry 14). Somehow, $PtCl_2$ did not show any catalytic activity for the reaction (Table 1, entry 15).[21]

***N*-Benzylation of amines 2 with benzyl alcohol (1a)**: Next, catalyst **III** was applied in the *N*-benzylation of amines **2**

Table 1. Screening of conditions for direct *N*-benzylation of **2a** with **1a**.[a]



Entry	Catalyst	Pt/Sn molar ratio[b]	Pt [mol %]	*T* [°C]	*t* [h]	**3aa**[c] [%]	**4a**[c] [%]
1	Pt/γ-Al_2O_3	–	0.25	145	24	14	19
2	Pt–Sn/γ-Al_2O_3 (**I**)	1:1	0.25	145	8	80	14
3	Pt–Sn/γ-Al_2O_3 (**II**)	1:2	0.25	145	8	94	6
4	**Pt–Sn/γ-Al_2O_3 (III)**	**1:3**	**0.25**	**145**	**8**	**97 (95)[d]**	**3**
5	Pt–Sn/γ-Al_2O_3 (**IV**)	1:5	0.25	145	8	94	6
6	Pt–Sn/γ-Al_2O_3 (**V**)	1:7	0.25	145	8	93	7
7	Pt–Sn/γ-Al_2O_3 (**VI**)	1:9	0.25	145	8	91	9
8	**III**	1:3	0.50	145	8	97	3
9	**III**	1:3	0.10	145	8	65	10
10	**III**	1:3	0.25	145	8[e]	98 (96)[d]	2
11	**III**	1:3	0.25	145	8[f]	90	10
12	**III**	1:3	0.25	110	24	67	10
13	**III**	**1:3**	**0.25**	**145**	**8[g]**	**5**	**46**
14	Pt–Sn/TiO_2	1:3	0.25	145	8	55	9
15	$PtCl_2$	–	0.25	145	24	n.d.[h]	n.d.

[a] Conditions: **1a** (1 mmol), **2a** (1 mmol), *o*-xylene (5 mL), mesitylene (20 mg, internal standard), 0.1 MPa N_2, in a sealed 15 mL Pyrex glass screw-cap tube. [b] The Pt content in all of the heterogeneous catalysts is 0.5 wt %. [c] Yield determined by GC analysis. [d] Isolated yield in parentheses. [e] Alcohol **1a** (1.1 mmol). [f] Reaction performed under an atmospheric N_2 balloon. [g] In air. [h] None detected.

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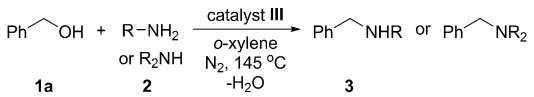
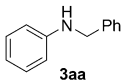
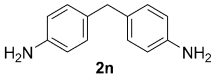
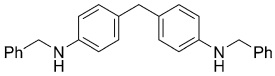
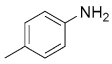
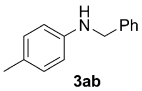
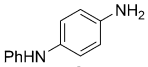
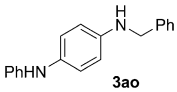
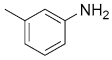
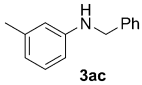
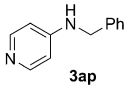
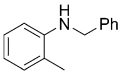
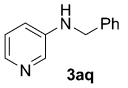
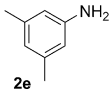
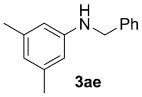
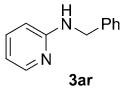
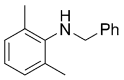
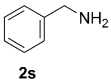
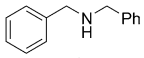
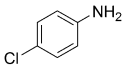
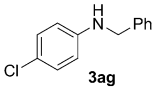
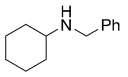
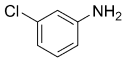
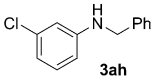
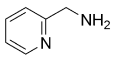
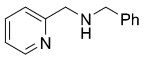
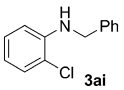
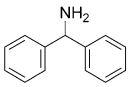
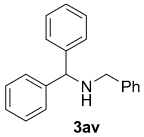
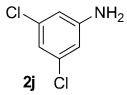
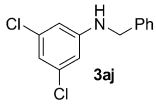
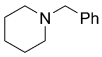
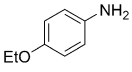
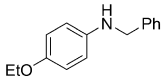
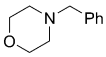
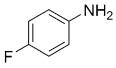
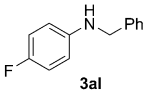
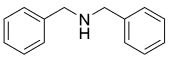
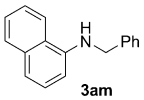
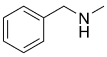
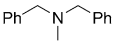
with **1a** under the optimized conditions (Table 2). A variety of anilines and pyridylamines reacted with **1a** to form the desired secondary amines **3aa–ar** in 90–99% yields, and only in the cases of sterically hindered 2,6-dimethylaniline (**2f**) and 4-PhNH-aniline (**2o**) were the products obtained in relatively low yields (82 and 74%, respectively; Table 2, entries 1–18). Various substituents, such as methyl, chloro, fluoro, ethoxy, and amino groups, can be tolerated under the

Table 2. Direct *N*-benzylation of amines **2** with alcohol **1a**.[a]



Entry	RNH_2 or R_2NH (**2**)	*t* [h]	RNHBn or R_2NBn (**3**)	Yield[b] [%]	Entry	RNH_2 or R_2NH (**2**)	*t* [h]	RNHBn or R_2NBn (**3**)	Yield[b] [%]
1	**2a**	8	 **3aa**	95	14[d]	 **2n**	48[c]	 **3an**	95
2	 **2b**	8	 **3ab**	90	15	 **2o**	48[c]	 **3ao**	74
3	 **2c**	8	 **3ac**	93	16	**2p**	48[c]	 **3ap**	92
4	**2d**	24	 **3ad**	91	17	**2q**	48[c]	 **3aq**	97
5	 **2e**	10	 **3ae**	94	18	**2r**	24	 **3ar**	99
6	**2f**	48[c]	 **3af**	82	19	 **2s**	8	 **3as**	95
7	 **2g**	10	 **3ag**	92	20	**2t**	8	 **3at**	80
8	 **2h**	24	 **3ah**	95	21	 **2u**	24[c]	 **3au**	72
9	**2i**	24[c]	 **3ai**	93	22	 **2v**	24	 **3av**	80
10	 **2j**	36[c]	 **3aj**	91	23	**2w**	24	 **3aw**	97
11	 **2k**	24	 **3ak**	97	24	**2x**	24	 **3ax**	97
12	 **2l**	24	 **3al**	96	25	 **3as**	24[c]	**3ay**	83
13	**2m**	36[c]	 **3am**	91	26	 **2y**	24[c]	 **3az**	90

[a] Conditions: **1a** (1 mmol), **2** (1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), *o*-xylene (5 mL), 145°C, 0.1 MPa N_2 atmosphere. [b] Yield of isolated product. [c] Pt (0.5 mol%). [d] Amine **2n** (0.5 mmol).

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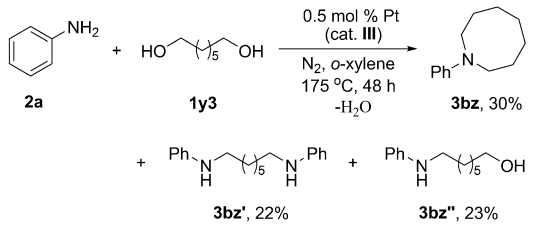
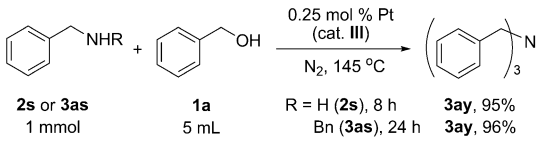
reaction conditions. Benzylamine (**2s**) reacted with **1a** to give dibenzylamine (**3as**) in 95% yield, whereas cyclohexylamine (**2t**), 2-(aminomethyl)pyridine (**2u**), and benzhydrylamine (**2v**) exhibited relatively low reactivity (Table 2, entries 20–22), which revealed unfavorable electronic and steric effects from the amine substrates. However, the reactions of aliphatic secondary amines **2w–y** and **3as** gave the corresponding tertiary amines in good to excellent yields (83–97%, Table 2, entries 23–26). It should be noted that diphenylamine and benzamide did not undergo *N*-benzylation with **1a** due to the weak nucleophilicity of their N–H bonds.[22]

***N*-Alkylation of aniline (2a) with alcohols 1**: *N*-Alkylation of **2a** with alcohols **1** was then explored (Table 3). Benzyl and 1-naphthylmethyl alcohols **1b–i** acted as very efficient alkylating reagents for **2a**; *N*-phenyl, *N*-benzyl, and *N*-phenyl-*N*-(1-naphthyl)methylamines **3ba–bh** were obtained in 90–98% yields (Table 3, entries 1–8). Both increasing the steric hindrance and introduction of a strong electron-withdrawing group on the benzyl alcohol lessened generation of the desired products, or led to an intermediate product, such as imine **4k** (Table 3, entries 10–12). Heteroarylmethyl alcohols **1n–q** and aliphatic alcohols **1r–x** also efficiently underwent N-alkylation with **2a** (Table 3, entries 13–23). Inter- and intramolecular N-alkylation of **2a** with diols successively occurred to form cyclic tertiary amines in 54–95% yields (Table 3, entries 24–29). In the case of 1,7-heptanediol (**1y3**), eight-membered cyclic tertiary amine **3bz** was obtained in 30% yield with concomitant formation of diamine $PhNH(CH_2)_7NHPh$ (**3bz'**, 22%) and aminoalcohol $PhNH(CH_2)_7OH$ (**3bz''**, 23%) as the minor products (Scheme 2); an unusual example of N-alkylation of amines with long-chain diols.[7d,11b,23]



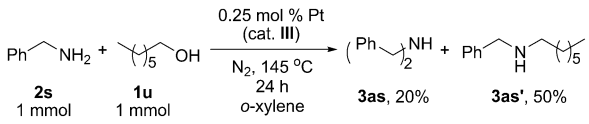
Scheme 2.

Unexpectedly, the present synthetic protocol worked more efficiently under solvent-free conditions. For example, the reactions of amines **2a** and **2b** with alcohol **1a** in a 1:1 molar ratio on a 10 mmol scale catalyzed by **III** (0.05 mol% Pt) afforded the desired products **3aa** and **3ab** in 95 and 97% yield, respectively, within 8–24 h. Moreover, N-alkylation of aniline with excessive alcohol or treatment of a primary or secondary amine in benzyl alcohol solvent efficiently produced tertiary amines (Scheme 3). These results suggest the potential application of the present synthetic methodology in the preparation of secondary and tertiary amines.



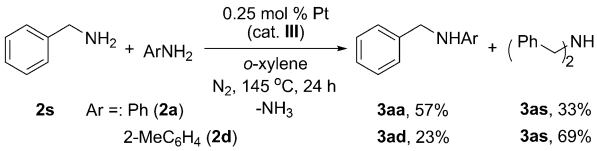
Scheme 3.

Deaminative self-coupling of aliphatic primary amines 2 to form secondary amines 3: N-Alkylation of **2s** with nonbenzylic alcohol *n*-heptanol (**1u**), formed a mixture of two secondary amines (Scheme 4). The production of **3as** reveals a deaminative self-coupling of **2s**.[7c,12h] Thus, intermolecular



Scheme 4.

deaminative coupling of benzylamines **2s** and **2s1–9** was carried out under the same conditions and the corresponding dibenzylamines were afforded in 87–96% yields (Table 4, entries 1–10). Electron-donating and electron-withdrawing substituents methyl, methoxy, chloro, and fluoro did not affect formation of the desired products. With long-chain (**2s10**, **2s11**) and cyclic (**2t**) aliphatic nonbenzyl primary amines as substrates, dialkylamines were also obtained in excellent yields (93–95%) (Table 4, entries 11–13). Notably, the reaction of an aliphatic primary amine with **2a** formed a mixture of two secondary amines due to easy deaminative self-coupling of aliphatic primary amines under the stated conditions (Scheme 5).



Scheme 5.

Direct synthesis of imines 4 from the tandem reactions of amines 2 with alcohols 1 in the presence of oxygen: As observed under an air atmosphere, catalyst **III** promoted the reaction of **2a** with **1a** to form imine **4a** (Table 1, entry 13). This revealed that oxygen, as an oxidant, protected the imine intermediate from further reduction to amine **3aa** in the catalytic cycle. The conditions for direct imine synthesis were screened in the reaction of **2a** with **1a** (Table 5). Imine **4a** was formed in a considerably good yield when the reaction mixture was heated at reflux in *o*-xylene under an air

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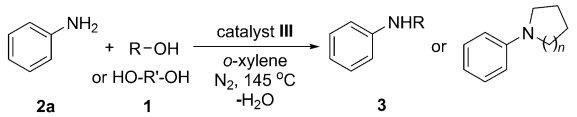
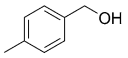
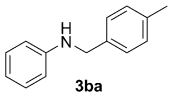
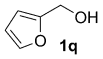
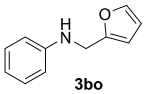
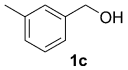
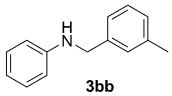
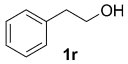
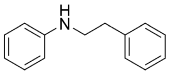
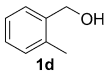
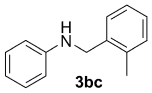
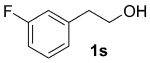
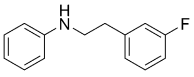
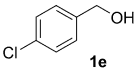
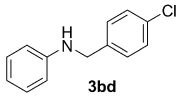
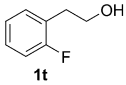
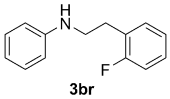
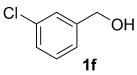
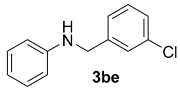
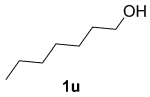
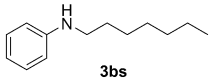
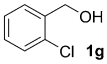
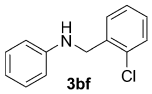
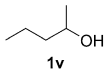
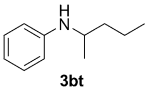
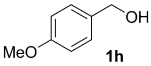
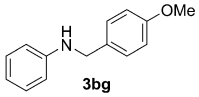
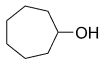
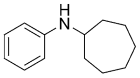
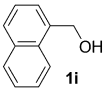
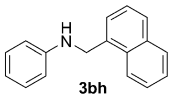
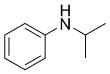
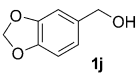
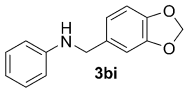
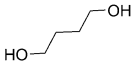
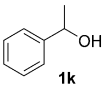
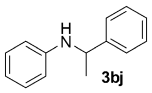
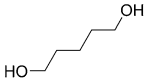
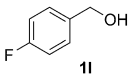
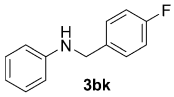
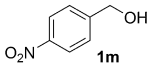
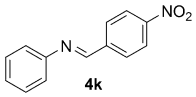
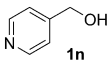
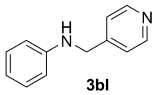
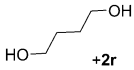
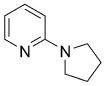
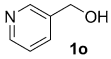
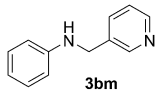
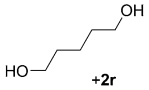
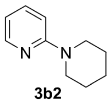
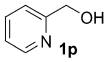
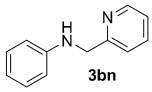
Table 3. Direct N-alkylation of **2a** with alcohols **1**.[a]



Entry	ROH or HOR'OH (**1**)	*t* [h]	PhNHR or PhNR′ (**3**)	Yield[b] [%]	Entry	ROH or HOR'OH (**1**)	*t* [h]	PhNHR or PhNR′ (**3**)	Yield[b] [%]
1	 **1b**	24	 **3ba**	96	16	 **1q**	36[c]	 **3bo**	73
2	 **1c**	24	 **3bb**	95	17	 **1r**	24	 **3bp**	88
3	 **1d**	24	 **3bc**	98	18	 **1s**	36[c]	 **3bq**	95
4	 **1e**	24	 **3bd**	90	19	 **1t**	36[c]	 **3br**	93
5	 **1f**	24	 **3be**	93	20	 **1u**	24	 **3bs**	93
6	 **1g**	24	 **3bf**	90	21	 **1v**	36	 **3bt**	89
7	 **1h**	24	 **3bg**	93	22	 **1w**	24	 **3bu**	90
8	 **1i**	24	 **3bh**	92	23	**1x**	24	 **3bv**	92
9	 **1j**	24[c]	 **3bi**	87	24	 **1y**	24[c]	**3bw**	95
10	 **1k**	36[c]	 **3bj**	84	25	 **1y1**	48[c]	**3bx**	80
11	 **1l**	48[c]	 **3bk**	70	26	$HO(CH_2)_6OH$ **1y2**	24[c]	**3by**	77
12	 **1m**	48[c]	 **4k**	64	27	$HO(CH_2)_7OHy$ **1y3**	48[c,e]	**3bz**	30
13	 **1n**	24[c]	 **3bl**	88	28	 **+2r**	36[c]	 **3b1**	54
14	 **1o**	24	 **3bm**	87	29	 **+2r**	36[c]	 **3b2**	57
15	 **1p**	36[c]	 **3bn**	77					

[a] Conditions: **2a** (1 mmol), **1** (1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), *o*-xylene (5 mL), 145°C, N_2 atmosphere. [b] Isolated yields. [c] Pt (0.5 mol%). [d] 4-$NO_2C_6H_4CH{=}NPh$ (**4k**). [e] 175°C.

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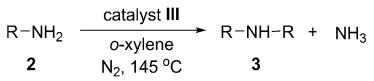
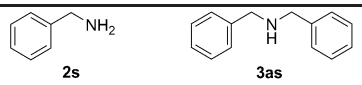
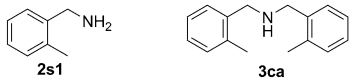
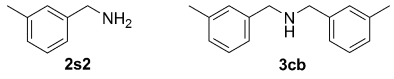
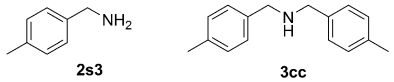
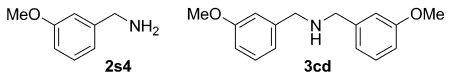
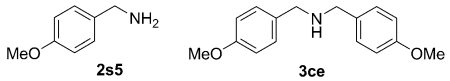
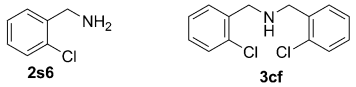
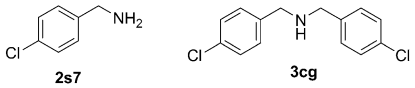
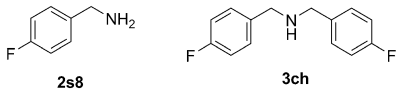
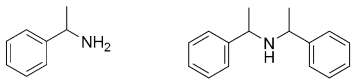
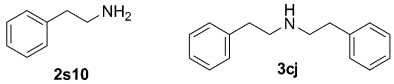
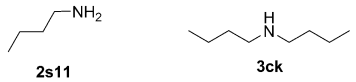
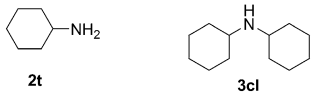
Table 4. Deaminative self-coupling of aliphatic primary amines **2** to form secondary amines **3**.[a]

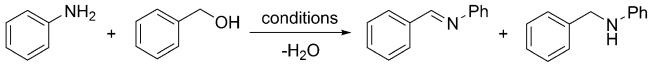


Entry	RNH_2 (**2**)	R_2NH (**3**)	Yield[b] [%]
1	 **2s**	**3as**	95
2	 **2s1**	**3ca**	93
3	 **2s2**	**3cb**	92
4	 **2s3**	**3cc**	93
5	 **2s4**	**3cd**	94
6	 **2s5**	**3ce**	95
7[c]	 **2s6**	**3cf**	93
8	 **2s7**	**3cg**	94
9	 **2s8**	**3ch**	96
10[c,d]	 **2s9**	**3ci**	87
11[c]	 **2s10**	**3cj**	93
12	 **2s11**	**3ck**	95
13[d]	 **2t**	**3cl**	95

[a] Conditions: **2** (1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), *o*-xylene (5 mL), 145°C, 24 h, 0.1 MPa N_2. [b] Isolated yield. [c] Pt (0.5 mol%). [d] 36 h.

atmosphere for an extended reaction time (Table 5, entries 2 and 3). However, an air or oxygen flow led to more formation of the secondary amine product **3aa** (Table 5, entries 5 and 6). Under an oxygen atmosphere, in toluene at reflux temperature, the desired imine product **4a** was selectively generated in a high yield (Table 5, entry 7) but ethylbenzene seemed to be the most suitable solvent for the reaction (Table 5, entries 8–13). Thus, it was found that catalyst **III** (0.3 mol% Pt) efficiently catalyzed the reaction of **2a** with **1a** at reflux temperature in ethylbenzene under an oxygen

Table 5. Screening of conditions for direct imine synthesis from the tandem reaction of **2a** with **1a**.[a]



Entry	Pt [mol%]	Solvent	Atmos.[b]	*t* [h]	Conv.[c] [%]	Selec.[c] **4a**/**3aa**
1	**0.25**	***o*-xylene**	**N_2**	**8**	**99**	**3:97**
2	0.25	*o*-xylene	air	8	51	90:10
3	0.25	*o*-xylene	air	24	81	81: 19
4	0.05	*o*-xylene	air	42	60	93: 7
5	0.25	*o*-xylene	air flow	8	99	30: 70
6	0.25	*o*-xylene	O_2 flow	8	99	51: 49
7[e]	0.25	PhMe	O_2	24	95	99: 1
8[f]	0.25	PhEt	air	24	83	90: 10
9[f]	0.50	PhEt	air	24	90	92: 8
10[f]	0.25	PhEt	O_2	24	99	99: 1
11[f]	**0.30**	**PhEt**	**O_2**	**24**	**>99**	**>99:<1**
12[f]	0.25	PhEt	O_2 flow	24	95	99:1
13[f]	0.30	PhEt	O_2 flow	24	>99	>99:<1

[a] Conditions: **1a** (1 mmol), **2a** (1 mmol), solvent (5 mL), 0.1 MPa O_2, air, or N_2, catalyst **III** (98 mg, 0.25 mol% Pt or 120 mg, 0.30 mol% Pt), 145°C, in a sealed 25 mL Pyrex glass screw-cap tube. [b] Atmosphere. [c] Conversion was determined by GC analysis. [d] Selectivity. [e] 110°C. [f] 138°C.

atmosphere—an oxygen gas flow was not necessary—to produce imine **4a**.[10c] An array of benzyl alcohols **1** were reacted with various anilines **2**; in most cases, nearly complete conversion was reached and 90–99% selectivity for the desired imine products **4** was obtained (Table 6). Only trace or small amounts of secondary amines (RNHR') were detected as the minor products. The steric hindrance in substrate **1k** led to lower selectivity for the desired product **4z1** (Table 6, entry 27). Aerobic couplings between aliphatic amine **2s** and alcohols **1a** or **1r** also occurred to give **4x** and **4z3**, respectively (Table 6, entries 24 and 29).

Tandem synthesis of imines 4 from the deamination of benzylamines 2 in the presence of oxygen: Due to the potential for deaminative coupling of aliphatic primary amines to form secondary amines (Table 4), aerobic deaminative coupling of benzylamines **2s** and **2s1–8** was carried out and efficiently afforded dibenzylimines **4x** and **4x1–8** in 86–96% yields (Table 7, entries 1–9). Steric hindrance in substrate **2s9** lessened formation of the desired product **4x9** (Table 7, entry 10), and aliphatic nonbenzylic amines **2s10** and **2t** underwent complicated conversion or showed no reactivity (Table 7, entries 11 and 12). Note that the reaction of benzylamine **2s3** with **2a** formed a mixture of two imines (Scheme 6), which revealed aerobic deaminative self- and cross-couplings between primary amines.

Catalyst recycling: Catalyst **III** was recycled for use in the *N*-benzylation of **2a** with **1a** (Table 8). For the first three runs, catalytic activity remained the same (Table 8, entries 1–3). In the fourth and fifth cycles, the catalytic activity was gradually decreased but 100% conversion and high

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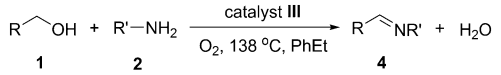
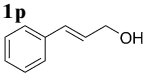
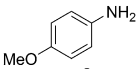
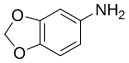
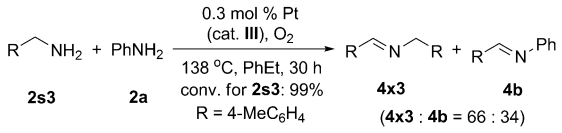
Table 6. Direct synthesis of imines **4** from the tandem reactions of amines **2** with alcohols **1**.[a]



Entry	RCH_2OH (**1**)	$R'NH_2$ (**2**)	*t* [h]	Conv. [%][b]	**4**	Selec. [%][b]
1	**1a**	**2a**	24	>99	**4a**	99
2	**1b**	**2a**	30	95	**4b**	93
3	**1c**	**2a**	30	97	**4c**	87
4	**1d**	**2a**	30	99	**4d**	92
5	**1e**	**2a**	30	>99	**4e**	97
6	**1f**	**2a**	30	>99	**4f**	96
7	**1g**	**2a**	30	>99	**4g**	97
8	**1h**	**2a**	30	>99	**4h**	96
9	**1i**	**2a**	24	>99	**4i**	86
10	**1j**	**2a**	30	>99	**4j**	96
11	**1m**	**2a**	30	>99	**4k**	96 (94)[c]
12	**1p**	**2a**	30[d]	>99	**4l**	90
13	 **1z**	**2a**	30	>99	**4m**	83
14	**1a**	**2b**	26	>99	**4n**	96 (94)[c]
15	**1a**	**2e**	30	99	**4o**	96
16	**1a**	**2g**	30	>99	**4p**	97
17	**1a**	**2h**	30	>99	**4q**	99
18	**1a**	**2i**	30	>99	**4r**	96
19	**1a**	**2k**	30	>99	**4s**	97
20	**1a**	 **2z**	30	>99	**4t**	99
21	**1a**	**2l**	30	>99	**4u**	98 (97)[c]
22	**1a**	 **2z1**	30	>99	**4v**	90
23	**1a**	**2m**	26	93	**4w**	98
24	**1a**	**2s**	26	>99	**4x**	90
25	**1b**	**2b**	30	99	**4y**	95
26	**1e**	**2g**	48	95	**4z**	96
27	**1k**	**2a**	30[d]	62	**4z1**	60
28	**1r**	**2a**	48[d]	70	**4z2**	60
29	**1r**	**2s**	30	99	**4z3**	90

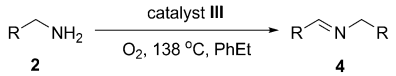
[a] Conditions: **1** (1 mmol), **2** (1 mmol), catalyst **III** (120 mg, 0.3 mol% Pt), PhEt (5 mL), 0.1 MPa O_2, in a sealed 25 mL Pyrex screw-cap tube. [b] Determined by GC analysis. [c] Isolated yields in parentheses. [d] Pt (0.5 mol%).

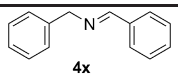
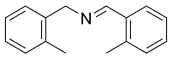
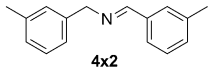
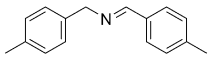
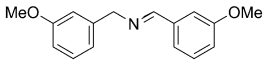
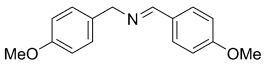
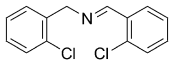
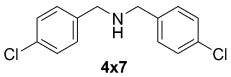
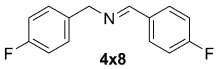
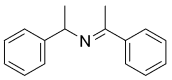
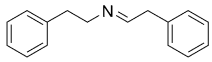


Scheme 6.

yields for the desired product were still reached by extension of the reaction time (Table 8, entries 4 and 5). After each reaction was complete, the catalyst was removed by centrifugation. Analysis of the supernatant by ICP-AES technology showed that no Pt was leaching into the liquid phase during the reaction. Furthermore, the supernatant did not exhibit any catalytic activity for the same reaction, confirmed by addition of equimolar amounts of **2a** and **1a** to the supernatant and treatment of the resultant mixture

Table 7. Tandem synthesis of imines **4** from the deamination of benzylamines in the presence of oxygen.[a]



Entry	RCH_2NH_2 (**2**)	Conv. [%][b]	RCH=NCH_2R (**4**)	Selec. [%][b]
1	**2s**	97[c]	 **4x**	96
2	**2s1**	99	 **4x1**	86
3	**2s2**	99	 **4x2**	88
4	**2s3**	99	 **4x3**	94
5	**2s4**	97	 **4x4**	90
6	**2s5**	97	 **4x5**	95
7	**2s6**	99[d]	 **4x6**	86
8	**2s7**	99[d]	 **4x7**	94
9	**2s8**	99	 **4x8**	96
10	**2s9**	91[d]	 **4x9**	71
11	**2s10**	99	 **4x10**	27[e]
12	**2t**	0	–	–

[a] Conditions: **2** (1 mmol), catalyst **III** (120 mg, 0.30 mol% Pt), PhEt (5 mL), 0.1 MPa O_2, 30 h, in a sealed 25 mL Pyrex screw-cap tube. [b] Determined by GC analysis. [c] Pt (0.15 mol%). [d] Pt (0.5 mol%). [e] Complicated mixture.

Table 8. Recycling catalyst **III** from the *N*-benzylation of **2a** with **1a**.[a]

Cycle	*t* [h]	Conv. **2a**[b] [%]	Yield of **3aa** [%][b]	Yield of **4a** [%][b]
1	8	100	97 (95)[c]	3
2	8	100	96	4
3	8	100	97 (95)[c]	3
4	8	86	78	8
	24	100	94	6
5	8	57	47	10
	30	100	95	5

[a] Conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), *o*-xylene (5 mL), 145 °C, 0.1 MPa N_2, in a 15 mL sealed Pyrex glass screw-cap tube. [b] Determined by GC analysis. [c] Isolated yield in parentheses.

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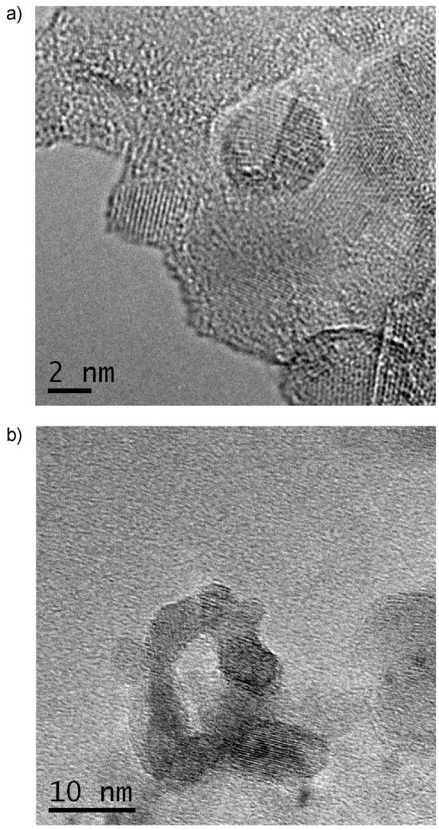

Figure 1. TEM micrographs of catalyst **III**: a) fresh catalyst prior to use; b) the catalyst after five cycles.

under the reaction conditions. The decrease in the catalytic activity after recycling is attributed to the aggregation of Pt nanoparticles on the γ-Al_2O_3 support during the reaction, which reduces the available bare surface of Pt particles catalytically active for the BH process. Transmission electron microscopy (TEM) images of fresh catalyst **III** and the used catalyst revealed that Pt particle size increased as the catalyst was recycled, from 3–5 nm in the fresh catalyst to 7–9 nm in the used catalyst after five cycles (Figure 1). Pulse chemisorption of CO experiments[24] demonstrated that Pt particle dispersion was decreased from 88.2% in the fresh catalyst to 78.3% in the used catalyst after five cycles, which also suggests aggregation of Pt particles during the course of the reaction. This is in agreement with the TEM observation and variation of the catalyst activity as shown in Table 8.

Conclusion

Efficient synthesis of secondary and tertiary amines from direct N-alkylation of primary and secondary amines with alcohols or deaminative self-coupling of primary amines has been successfully realized by using a heterogeneous bimetallic Pt–Sn/γ-Al_2O_3 catalyst in a borrowing-hydrogen strategy. In the presence of oxygen, imines were also efficiently prepared from the tandem reactions of amines with alcohols or between two amines. This catalyst can be easily recycled and has exhibited very high catalytic activity toward a wide array of amine and alcohol substrates, which suggests its potential for application in the production of secondary and tertiary amines and imines.

Experimental Section

General considerations: All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Reaction solvents were dried and distilled prior to use by literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift (δ) values are referenced to TMS ($\delta = 0.00$ ppm) or $CDCl_3$ (^{1}H: $\delta = 7.26$ ppm; ^{13}C: $\delta = 77.16$ ppm). HRMS analyses were measured on a Waters GC-TOF CA156 mass spectrometer. All the melting points are uncorrected. Analytical TLC plates (Sigma–Aldrich silica gel 60_{F200}) were viewed under UV light (254 nm). Chromatographic purifications were performed on SDZF silica gel 160. The known compounds were identified by comparison of their NMR spectra with the reported data or of their GC traces with those of authentic samples. The spectroscopic features of these known compounds are in good agreement with those reported in the literature.

Typical procedure for the direct N-alkylation of amines 2 with alcohols 1 (3aa): Under nitrogen atmosphere, **1a** (108 mg, 1 mmol), **2a** (93 mg, 1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), and *o*-xylene (5 mL) were added to a 15 mL Pyrex glass screw-cap tube. The resultant mixture was stirred in the sealed tube at 145°C for 8 h. The mixture was cooled to ambient temperature, then the catalyst was removed by centrifugation and washed with Et_2O (2×5 mL). The combined supernatant was concentrated to approximately 0.5 mL under reduced pressure and then subject to purification by silica gel column chromatography (petroleum ether (60–90°C)/EtOAc=20:1) to afford **3aa** as a colorless liquid (174 mg, 95%).

Typical procedure for N-alkylation of amines 2 in alcohol solvents (3ay): Under nitrogen atmosphere, **1a** (5 mL, 47.8 mmol), **2s** (107 mg, 1 mmol), and catalyst **III** (98 mg, 0.25 mol% Pt) were added to a 15 mL Pyrex glass screw-cap tube. The resultant mixture was stirred in the sealed tube at 145°C for 8 h. The mixture was cooled to ambient temperature, then the catalyst was removed by centrifugation and washed with Et_2O (2× 5 mL). The combined supernatant was concentrated to approximately 0.5 mL under reduced pressure and then subject to purification by silica gel column chromatography (petroleum ether (60–90°C)/EtOAc=20:1) to afford tribenzylamine **3ay** as a white solid (273 mg, 95%). M.p. 91–92°C.

Typical procedure for deaminative self-coupling of aliphatic primary amines 2 (3as): Under nitrogen atmosphere, **2s** (107 mg, 1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), and *o*-xylene (5 mL) were added to a 15 mL Pyrex glass screw-cap tube. The resultant mixture was stirred in the sealed tube at 145°C for 8 h. The mixture was cooled to ambient temperature, then the catalyst was removed by centrifugation and washed with Et_2O (2×5 mL). The combined supernatant was concentrated to approximately 0.5 mL under reduced pressure and then subject to purification by silica gel column chromatography (petroleum ether (60–90°C)/EtOAc=20:1) to afford dibenzylamine **3as** as a colorless liquid (94 mg, 95%).

Typical procedure for synthesis of imines from the reactions of amines 2 with alcohols 1 under oxygen atmosphere (4a): Benzyl alcohol **1a** (108 mg, 1 mmol), aniline **2a** (93 mg, 1 mmol), catalyst **III** (120 mg, 0.3 mol% Pt), and ethylbenzene (5 mL) were added to a 25 mL Pyrex glass screw-cap tube. The atmosphere was replaced by 0.1 MPa oxygen and the reactor was sealed. The resultant mixture was then stirred at 138°C for 24 h. The mixture was cooled to ambient temperature, then the catalyst was removed by centrifugation and washed with Et_2O (2× 5 mL). The combined supernatant was subject to GC analysis: conversion

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of **1a** > 99%; selectivity for imine **4a** = 99%. To isolate **4a**, the combined supernatant was concentrated to approximately 0.5 mL under reduced pressure and then subject to purification by silica gel or alumina column chromatography (petroleum ether (60–90°C)/EtOAc = 20:1) to afford imine **4a** (177 mg, 97%).

Typical procedure for catalyst recycling: Under nitrogen atmosphere, **1a** (108 mg, 1 mmol), **2a** (93 mg, 1 mmol), catalyst **III** (98 mg, 0.25 mol% Pt), and *o*-xylene (5 mL) were added to a 15 mL Pyrex glass screw-cap tube. The resultant mixture was stirred in the sealed tube at 145°C for 8 h. The mixture was cooled to ambient temperature, then centrifuged in the reaction tube and decanted. The precipitate was washed with Et_2O (2×5 mL) and *n*-hexane (3×1 mL) with repeated centrifugation/decantation after each washing. The combined supernatant was subject to GC analysis and then concentrated to approximately 0.5 mL under reduced pressure. Purification by silica gel column chromatography (petroleum ether (60–90°C)/EtOAc = 20:1) afforded amine **3aa** as a colorless liquid (174 mg, 95%). The recovered catalyst was left in the tube reactor, dried at 60°C/2 mmHg for 2 h, and then reused in a subsequent reaction of **2a** with **1a**.

Acknowledgements

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