Synthetic Methods

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Platinum-Catalyzed Direct Amination of Allylic Alcohols with Aqueous Ammonia: Selective Synthesis of Primary Allylamines**

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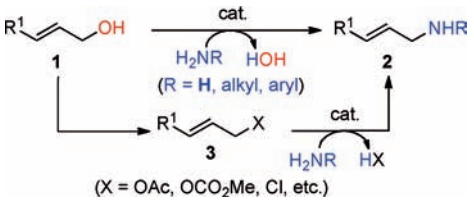
Ammonia has been one of the most important chemical feedstocks for the chemical industry since the discovery of the Harber–Bosch process.[1] Direct synthesis of nitrogen-containing compounds from ammonia is the most desirable synthetic route, and recent achievements regarding the direct use of ammonia have been reported.[2,3] Among nitrogen-containing chemicals, allylamines are ubiquitous and prevalent in various biologically active compounds,[4,5] and are valuable synthetic intermediates for a wide range of organic compounds.[5,6] The direct catalytic substitution of allylic alcohols with ammonia (Scheme 1, **1**→**2**, R = H) is considered



Scheme 1. Direct (**1**→**2**) and two-step (**1**→**3**→**2**) syntheses of allylamines **2** from allylic alcohols **1**.

to be the most rational synthetic protocol for primary allylamines because of the ready availability of allylic alcohols and the low cost of ammonia, and it is attractive in terms of its environmental benefit because water is the sole by-product.[7] The synthetic strategy to directly use ammonia as a nucleophile has been applied for the amination of allylic esters and carbonates (**3**→**2**) using a palladium catalyst as reported by Kobayashi et al.,[8] and the enantioselective amination of allylic carbonates using a chiral iridium catalyst as reported by Hartwig et al.[9] Recently, Carreira et al. reported that optically active allylamines were prepared by the iridium-catalyzed stereospecific substitution reaction of optically active branched allylic alcohols with sulfamic acid as an ammonia equivalent.[10] To the best of our knowledge, ammonia has never been used for the direct transformation of allylic alcohols into primary allylamines (**1**→**2**, R = H) because the nucleophilicity of ammonia is much lower than that of alkylamines.

Direct amination of allylic alcohols is difficult to achieve even when alkylamines (R = alkyl) and related nitrogen nucleophiles are used, because of the poor leaving ability of the hydroxy group. Thus, in the earliest stages of development, transition-metal-catalyzed amination of allylic alcohols exploited activated allylic alcohols,[11] and stoichiometric or catalytic amounts of an activator were required for the direct aminations of allylic alcohols.[12,13] Since the pioneering work by Ozawa and Yoshifuji,[14a] some palladium[14] catalyst systems without an activator were reported to facilitate the direct amination of allylic alcohols **1** with alkyl- and arylamines. We also demonstrated that a platinum catalyst system, [Pt(cod)Cl_2] (cod = 1,5-cyclooctadiene), and a large bite-angle ligand, DPEphos or Xantphos, under microwave irradiation conditions promotes the direct catalytic amination of allylic alcohols with alkyl- and arylamines with high monoallylation selectivity.[15] We report herein the first direct amination of allylic alcohols with ammonia via a π-allylmetal intermediate without the use of an activator.

In our search for efficient catalytic conditions, we chose the allylic amination reaction of cinnamyl alcohol (**1a**) with degassed aqueous ammonia[16] as a test reaction, and the results are summarized in Table 1. Under the optimized reaction conditions for alkylamine,[15a] we performed the reaction using 28% aqueous ammonia[16] (ca. 20 equiv, 1:5 (v/v) mixture of aq. ammonia and 1,4-dioxane) at 100 °C for 24 h, and the corresponding linear monoallylated amine **2a** was obtained in 60% yield along with bisallylated amine **4a** (**2a**/**4a** = 82:18) with water as the sole by-product (entry 1). The formation of branched allylamines was not detected in the ^{1}H NMR spectrum of the crude reaction mixture. Because product **2a** has much higher nucleophilicity than ammonia and thus over-reaction of **2a** with **1a** to give **4a** proceeds more readily, the monoallylation selectivity was lower than that when alkylamine was used as the nucleophile.[15a] This moderate monoallylation selectivity was improved to 90:10 by increasing the amount of ammonia (60 equiv) to afford the desired product **2a** in 74% yield (entry 3). Unexpectedly, the reaction with excess amounts of ammonia resulted in a lower

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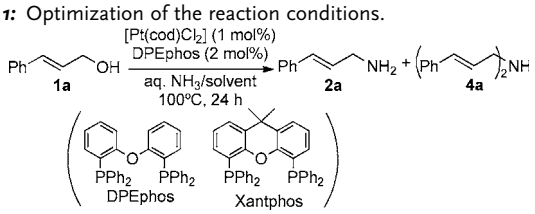
Table 1: Optimization of the reaction conditions.



Entry[a]	Solvent	aq. NH_3/solvent (equiv of NH_3)[16]	**2a** Yield [%][b]	**2a**/**4a**[b]
1	1,4-dioxane	1:5 (20)	60	82:18
2	1,4-dioxane	1:2 (40)	71	89:11
3	1,4-dioxane	1:1 (60)	74	90:10
4	1,4-dioxane	2:1 (80)	51	94:6
5[c]	1,4-dioxane	1:1 (60)	n.d.[d]	–
6[e]	1,4-dioxane	1:1 (60)	34	94:6
7[e]	1,4-dioxane	1:1 (60)	29	97:3
8	THF	1:1 (60)	52	91:9
9	DME	1:1 (60)	59	92:8
10	toluene	1:1 (60)	n.d.[d]	–
11	CH_3CN	1:1 (60)	27	96:4
12	DMSO	1:1 (60)	30	94:6
13	DMF	1:1 (60)	4	80:20
14	MeOH	1:1 (60)	71	93:7
15	–	– (120)	7[f]	93:7
16	1,4-dioxane/MeOH	3:2:1 (60)	79 (72)[g]	91:9
17[h]	1,4-dioxane/MeOH	3:2:1 (60)	69	92:8

[a] Reaction conditions: **1a** (0.5 mmol), $[Pt(cod)Cl_2]$ (1 mol%), DPEphos (2 mol%), 28% aq. NH_3[16] and solvent (total volume 6.0 mL), 100°C in sealed tube. [b] Determined by ^1H NMR spectrum of the crude reaction mixture. [c] Reaction temperature was 80°C. [d] Not detected. [e] Xantphos was used instead of DPEphos. Pt/L = 1:2 (entry 6) and 1:1 (entry 7). [f] **1a** was recovered in 92% yield. [g] Yield of isolated product after Boc protection.[18] [h] 0.5 mol% of catalyst was used. DME = ethyleneglycol dimethyl ether, DMF = *N*,*N*′-dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

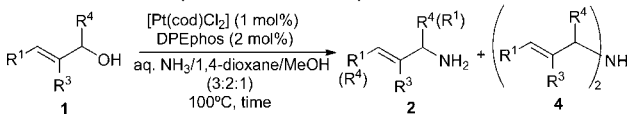
yield because of the partial deactivation of the platinum catalyst at a higher concentration of ammonia (entry 4). At a lower reaction temperature (80°C), no reaction occurred (entry 5). Under the same reaction conditions as those used for entry 3, the Pt/Xantphos catalyst systems (Pt/L = 1:2 and 1:1) were less efficient and gave **2a** in poor yield (entries 6 and 7). We then examined the solvent effects relative to a 1:1 (v/v) ratio of aqueous ammonia and solvents. In THF and DME, **2a** was obtained in moderate yields; 52% and 59%, respectively (entries 8 and 9). In toluene, no reaction proceeded because of the biphasic reaction mixture (entry 10). Coordinative solvents such as acetonitrile and DMSO afforded the products in lower yields (entries 11 and 12). In DMF, *N*,*N*-dimethyl-3-phenylprop-2-en-1-amine was formed as the major product through transamidation of DMF with ammonia, and a trace amount of the desired primary allylamine was detected in the crude reaction mixture (entry 13).[15b] In protic methanol media, the results were similar (entry 14) to those obtained in 1,4-dioxane. Other alcohols were less effective than MeOH in terms of the yield of **2a**.[17] The reaction in aqueous ammonia without organic solvent resulted in a very low yield of **2a** along with recovered starting material (92%; entry 15). It is intriguing that the Pt/DPEphos in the mixed solvent system of aqueous ammonia, 1,4-dioxane, and MeOH in a 3:2:1 (v/v/v) ratio provided the best yield (79%) with high monoallylation selectivity (**2a**/**4a** = 91:9; entry 16); these reaction conditions were finally selected as the best set of reaction conditions.[18] The reaction using only 0.5 mol% of catalyst also proceeded smoothly, though the yield of **2a** was slightly lower (entry 17).

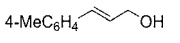
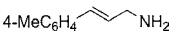
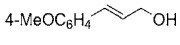
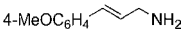
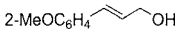
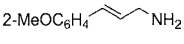
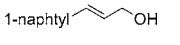
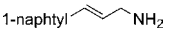
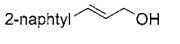
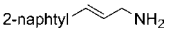
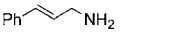
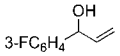
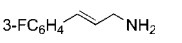
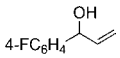
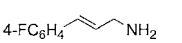
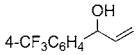
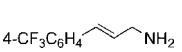
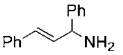
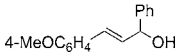
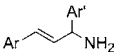
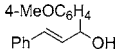
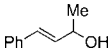
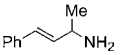
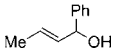
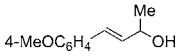
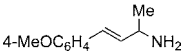
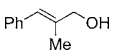
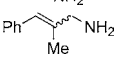
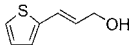
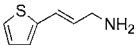
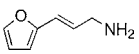
With the optimized conditions in hand, we examined the scope of the allylic alcohols **1**, and the results are summarized in Table 2.[18] Direct amination of a series of cinnamyl alcohol derivatives (**1b–f**) with aqueous ammonia afforded the corresponding primary monoallylamines **2b–f** with high yield and high selectivity (entries 1–5). Notably, the branched allylic alcohol **1g** was efficiently converted into primary allylamine **2a** with the same **2**/**4** distribution (entry 6) as observed for the reaction of **1a** (entry 16, Table 1).[18] Other branched allylic alcohols (**1h–j**) also gave comparable results (entries 7–9). Sterically congested 1,3-disubstituted allylic alcohols **1k–p** were good substrates for the present catalysis. (*E*)-1,3-Diphenylprop-2-en-1-ol (**1k**) was readily converted into 1,3-diphenylallylamine (**2k**) in excellent yield, and, notably, the corresponding bisallylated product **4k** was not detected by ^1H NMR or CI-MS analysis of the crude reaction mixture (entry 10). The excellent high monoallylation selectivity observed for **1k** originated from the selective attack of the smaller nucleophile ammonia on the 1,3-diphenyl π-allylplatinum intermediate, where the large bite angle of the diphosphine ligand DPEphos produced a congested environment around the Pt center, compared with the corresponding monoallylated amine **2k**. Similarly, the amination of (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (**1l**) and (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol (**1m**) produced identical monoallylated amines **2l** as a regioisomeric mixture with the same ratio (53:47; entries 11 and 12).

Direct catalytic amination of alkyl-substituted allylic alcohol remains a challenging task because of its low reactivity and the potential risk of β-hydride elimination. In our previous platinum catalysis using alkyl- and arylamines as a nucleophile, such undesired side reactions were prevented by changing the solvent from 1,4-dioxane to DMF and lowering the reaction temperature to 50°C. As shown in Table 1, however, the present platinum-catalyzed amination with ammonia could not employ either DMF or low temperature conditions. Fortunately, under the optimized reaction conditions shown in Table 2, reactions of (*E*)-4-phenylbut-3-en-2-ol (**1n**) and (*E*)-1-phenylbut-2-en-1-ol (**1o**) resulted in the good conversion into the same monoallylated amine **2n** with the same high **2**/**4** selectivity (> 99:1; entries 13 and 14).[17] The reaction of (*E*)-4-(4-methoxyphenyl)but-3-en-2-ol (**1p**) with ammonia also proceeded efficiently to give the corresponding monoallylated amine **2p** in 70% yield without the formation of the bisallylated amine **4p**. Although the cyclic allylic alcohols **1q** (entry 16) and the β-substituted **1r** (entry 17) were less reactive substrates, good yields were obtained when using 3 mol% of the catalyst.

Furthermore, highly unstable thiophene- and furan-substituted allylic alcohols **1s** and **1t**, respectively (entries 18 and 19), were also successfully converted into the corresponding primary amines without decomposition. Overall, this platinum catalytic system provides a new protocol for the direct

Table 2: Platinum-catalyzed direct amination of various allylic alcohols with aqueous ammonia.



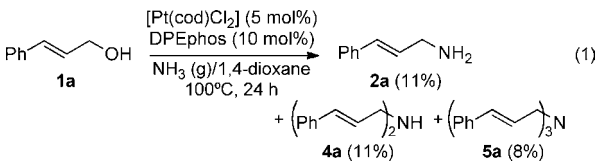
Entry[a]	1		2		*t* [h]	2 Yield [%][b]	2/4[b]
1		**1b**		**2b**	24	76 (68)	93:7
2		**1c**		**2c**	48	78 (70)	91:9
3		**1d**		**2d**	48	73 (68)	91:9
4		**1e**		**2e**	48	77 (70)	94:6
5		**1f**		**2f**	48	75 (69)	91:9
6		**1g**		**2a**	24	77 (66)	91:9
7		**1h**		**2h**	24	77 (66)	93:7
8		**1i**		**2i**	24	81 (71)	91:9
9		**1j**		**2j**	24	71 (69)	91:9
10		**1k**		**2k**	48	88 (78)	>99:1[c]
11[d]		**1l**		**2l**[e]	65	84 (72)	>99:1[c]
12[d]		**1m**		**2l**[e]	65	84	>99:1[c]
13		**1n**		**2n**	48	80 (65)	>99:1[c]
14		**1o**		**2n**	48	71 (61)	>99:1[c]
15		**1p**		**2p**	48	70 (62)	>99:1[c]
16[f]		**1q**		**2q**	64	78 (66)	>99:1[c]
17[f]		**1r**		**2r**[g]	48	76 (70)	>99:1[c]
18[f]		**1s**		**2s**	48	72 (67)	92:8
19		**1t**		**2t**[h]	13	(64)	94:6

[a] Reaction conditions: **1** (0.5 mmol), [Pt(cod)Cl_2] (1 mol%), DPEphos (2 mol%), 28% aq. NH_3,[16] 1,4-dioxane and MeOH (3:2:1, total volume 6.0 mL), 100°C in sealed tube. Starting material **1** was consumed except for those reaction in entries 5 and 17. [b] Determined by ^{1}H NMR spectrum of the crude reaction mixture. The number in parenthesis is the yield of the isolated product after Boc protection.[18] [c] **4** was not detected by either ^{1}H NMR or CI-MS analysis of the crude reaction mixture. [d] 2.5 mol% of catalyst was used. [e] A mixture of regioisomers (53:47) was obtained. [f] 3.0 mol% of catalyst was used. [g] *E*/*Z* mixture (88:12) was obtained. [h] *E*/*Z* mixture (95:5) was obtained.

amination of allylic alcohols with aqueous ammonia with a wide substrate scope, thus offering an efficient, direct access to primary allylic amines in an atom-economical and environmentally benign way.

As shown in Tables 1 and 2, reactions using the terminal allylic alcohol **1a** and internal allylic alcohol **1g**, and reactions using **1n** and **1o**, respectively, gave almost identical results. These facts provide insight into the mechanism of the platinum-catalyzed direct amination of allylic alcohols with ammonia that proceeded via a π-allylplatinum intermediate.

In the platinumt-catalyzed direct amination, the use of aqueous ammonia is essential for achieving the high yield of **2a** and high monoallylation selectivity. The reaction of **1a** with gaseous ammonia dissolved in 1,4-dioxane afforded **2a** in poor yield (11%) along with a bisallylated amine **4a** (11%) and a tertiary amine **5a** [8%; Eq. (1)]. In contrast to our previous observation that amine salts (NH_2R·HCl) activated the hydroxy group of the allylic alcohols, the addition of NH_4Cl (2 equiv to substrate) to the present aqueous con-



(1)

ditions did not significantly improve catalytic activity. Thus, it is likely that the aqueous conditions contributed to the hydrogen bonding effects of water to activate the hydroxy group of allylic alcohols.[14b]

In summary, we developed the first direct catalytic amination of allylic alcohols with aqueous ammonia using a Pt/DPEphos catalyst system without the prior activation of the allylic alcohol. In this new protocol under aqueous conditions, a variety of primary allylamines were directly synthesized from the corresponding allylic alcohols with high monoallylation selectivity. Additional investigation of the scope of the syntheses of highly functionalized bioactive natural and unnatural compounds and application to enantioselective variants, one-pot sequential reaction, and flow system are ongoing in our group.

Experimental Section

Degassed aq. ammonia (3 mL) was added to a solution of allylic alcohol **1k** (105 mg, 0.500 mmol), [Pt(cod)Cl_2] (1 mol%), and DPEphos (2 mol%) in a mixed solvent (3 mL) of 1,4-dioxane and MeOH in 2:1 proportion. The reaction mixture was stirred in a stainless steel autoclave at 100°C for 48 h. The reaction mixture was cooled and then an excess of ammonia was released. The resulting reaction mixture was diluted with a saturated aq. $NaHCO_3$ solution (10 mL), and then organic compounds were extracted with CH_2Cl_2 (4×15 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum (Caution: some primary amines are too volatile to be evaporated under prolonged vacuum condition) to give the crude reaction mixture, which was analyzed by ^{1}H NMR spectroscopy (in C_6D_6) using phenanthrene as an internal standard. The yield of the corresponding monoallylamine **2k** was determined to be 88% (selectivity >99%) in the crude reaction mixture. Then, the crude reaction mixture was dissolved in CH_2Cl_2 (4 mL), cooled to 0°C, and added to a solution of Boc anhydride (164 mg, 0.750 mmol) and Et_3N (175 μL, 1.25 mmol) in CH_2Cl_2 (4 mL). After stirring for 24 h at room temperature, the reaction mixture was diluted with $NaHCO_3$ and extracted with CH_2Cl_2 (3× 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 19:1) to afford the corresponding *N*-Boc-protected monoallylamine **6k** in 78% yield (120 mg, 0.388 mmol) as a white solid.

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[16] Commercial aqueous ammonia solution (28%) was degassed by passing argon through the solution for approximately 15 min prior to use, and the ammonia concentration was changed from 11.4 M to 10.4 M. Without the degassing process, the platinum catalyst was partially decomposed.

[17] See the Supporting Information for details.

[18] Primary amines are highly volatile and can be isolated in lower yields. Because these free amines were obtained as crude reaction mixtures under aqueous conditions, we isolated the monoallylamines **2a**–**t** as their N-Boc derivatives. In the case of **2a**, **2k**, and **2n**, they were also isolated as their hydrochloride salts.

