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Gallium Trichloride Catalyzed Hydroamination of Alkynes: Scope, Limitation, and Mechanistic Studies by DFT

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The successful application of gallium trichloride as a catalyst for the intermolecular hydroamination of alkynes with aromatic amines is reported. The reaction is effective with many aniline derivatives and shows exclusive selectivity for the Markovnikov products. The mechanism of the transformation was investigated by DFT calculations and a plausible pathway is proposed.

Introduction

The hydroamination of alkenes, alkynes, and related unsaturated substrates is an attractive strategy for the preparation of amines, enamines, and imines, which are valuable and industrially important bulk chemicals, specialty chemicals, and pharmaceuticals.[1] Because of the high activation barrier of the hydroamination reaction,[2] the development of catalytic transformations is necessary and has been the focus of numerous studies during the last two decades.[3] A plethora of catalytic systems are known to effect such transformations, including those based on alkali and alkaline-earth metals,[4] rare-earth metals and actinides,[5] group 4 and 5 metals,[3a,6] late-transition metals of groups 8–12,[7] bases,[8] Brønsted acids,[9] and various types of heterogeneous catalysts.[10] However, the potential of group 13–15 metal-based hydroamination catalysts has received less attention. For example, there are only a very limited number of reports available on the use of group 13–15 metal-based catalysts, for example, $InBr_3$,[11] $GaCl_3$,[12] $Bi(OTf)_3$,[13] aluminium compounds,[14] and $BiCl_3$,[15] for the hydroamination of alkenes and little attention has been paid to the use of these catalysts for the hydroamination of alkynes.[16]

Two different mechanisms have been proposed for the hydroamination of alkenes and alkynes: 1) The activation of amines and 2) the activation of alkenes or alkynes. The amine activation mechanism has been well established for alkali and alkaline-earth metals, lanthanides, and group 4 and 5 metals. Depending on the catalyst used, both mechanisms have been suggested for the hydroamination reaction catalyzed by late-transition-metal complexes.

The accepted hydroamination pathway mediated by alkali and alkaline-earth metals and lanthanides involves C–C multiple bond insertion into a M–N bond followed by rapid protonolysis by other amine substrates.[4,5] The hydroamination reaction catalyzed by group 4 and 5 metals occurs by the formation of an imido species, which reacts further with the C–C multiple bond through a [2+2] cycloaddition to form an azametallacyclobutene species, which is protonolyzed by other amine substrates to release the product.[17] For late-transition-metal-catalyzed hydroamination reactions, the activation of alkenes or alkynes occurs by coordination of the alkene or alkyne to the metal to give a coordination complex, which is subsequently subjected to nucleophilic attack by the amine;[18] the activation of amines can be achieved by oxidative addition of an amine to the metal center, then a C–C unsaturated bond is inserted into the M–N bond, and the subsequent reductive elimination of the metal complex generates the hydroamination product.[19] The Lewis acid–base interaction between $BiCl_3$ and amine substrates has been proposed as the key initiation step for the $BiCl_3$-catalyzed hydroamination reaction of norbornene with aromatic amines,[15] whereas C=C double-bond activation by the interaction between $Bi(OTf)_3$ and the diene to generate an allyl cationic species, which is subsequently trapped with an amide, has been postulated as the mechanism for $Bi(OTf)_3$-catalyzed hydroamination of 1,3-dienes with carbamates, sulfonamides, and carboxamides.[13]

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None of the above-described mechanisms has been explored for the $GaCl_3$- or $InBr_3$-catalyzed hydroamination of alkenes with sulfonamides, neither have mechanisms for the hydroamination of alkynes catalyzed by group 13–15 metal complexes been reported. Our previous studies indicated that $BiCl_3$ and $AlCl_3$ are efficient catalysts for the hydroamination of alkenes with aromatic amines.[14a,15] As a continuation of our ongoing efforts on the hydroamination of alkenes catalyzed by group 13–15 metal complexes, and also driven by an impetus for exploring the mechanisms of the hydroamination of alkenes and alkynes catalyzed by group 13–15 metal complexes, we have investigated the hydroamination of alkynes catalyzed by several group 13–15 metal complexes. Gratifyingly, $GaCl_3$ was found to be an efficient catalyst. Herein we report the first successful use of $GaCl_3$ as a catalyst for the intermolecular hydroamination of alkynes. Mechanistic studies were performed by DFT calculations and a plausible mechanism for the reaction is proposed based on the results of the calculations, which support the C–C activation pathway. The regioselectivities of the reactions as well as the reactivities of the different amine substrates can be well explained by the proposed mechanism.

Results and Discussion

Optimization of the Conditions for the Gallium Trichloride Catalyzed Hydroamination Reaction

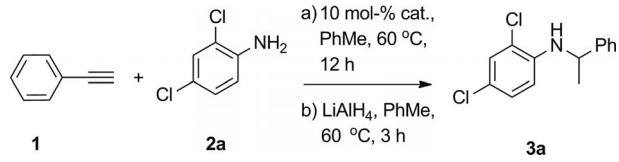
An initial catalyst screening was performed for the reaction between phenylacetylene (**1**) and 2,4-dichloroaniline (**2a**) in toluene as solvent by using a variety of group 13–15 metal catalysts (Table 1). Typically, a reaction mixture consisting of 10 mol-% of catalyst, **1**, **2a**, and toluene was sealed in a pressure tube and heated in an oil bath at 60 °C. Because the resulting imines were not stable to column chromatography, the hydroamination products were directly reduced to amines with $LiAlH_4$ in toluene for 3 h. The product **3a** was isolated by flash chromatography. The results are summarized in Table 1.

As we can see from Table 1, $GaCl_3$ stands out as an excellent catalyst for this reaction, generating 70% of **3a** (Table 1, entry 2). The other group 13 metal compounds either gave a trace amount (Table 1, entry 1) or a decreased yield of **3a** (Table 1, entry 3). The group 14 metal complexes, $SnCl_2$ (Table 1, entry 4), $SnCl_4$ (Table 1, entry 5), and $PbCl_2$ (Table 1, entry 6), did not give the expected products. Likewise, the group 15 metal compounds $SbCl_3$ and $BiCl_3$ were not catalytically active (Table 1, entries 7 and 8), which contrasts with the $BiCl_3$-catalyzed hydroamination of norbornene, in which $BiCl_3$ effectively catalyzed the hydroamination reaction.[15]

Pleasingly, the hydroamination of **1** with **2a** proceeded with very good regioselectivity, and 100% Markovnikov selectivity was observed for all group 13 metal catalysts.

Following the catalyst screening, we were interested in optimizing the reaction conditions of the hydroamination reactions catalyzed by $GaCl_3$. The effects of solvent, alkyne, catalyst loading, and temperature on the yields of the hydroamination reactions were examined and the results are presented in Table 2.

Table 1. Hydroamination reaction between phenylacetylene (**1**) and 2,4-dichloroaniline (**2a**) catalyzed by group 13–15 metal complexes.[a]

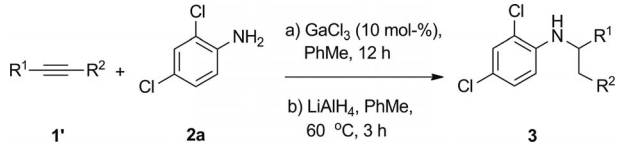


1 **2a** **3a**

Entry	Catalyst	Yield of **3a** [%][b]
1	$AlCl_3$	trace
2	$GaCl_3$	70
3	$InCl_3$	51
4	$SnCl_2$	0
5	$SnCl_4$	0
6	$PbCl_2$	0
7	$SbCl_3$	0
8	$BiCl_3$	0

[a] Reaction conditions: **1** (3 mmol), **2a** (4.5 mmol), catalyst (10 mol-%), toluene (4 mL). [b] Isolated yield after reduction by $LiAlH_4$.

Table 2. Reactions of 2,4-dichloroaniline (**2a**) with alkynes **1′** catalyzed by $GaCl_3$ under different conditions.[a]



1′ **2a** **3**

Entry	Alkyne	Catalyst loading [mol-%]	Solvent	T [°C]	Product	Yield [%][b]
1	PhC≡CH	10	THF	60	**3a**	66
2	PhC≡CH	10	CH_3CN	60	**3a**	trace
3	PhC≡CH	10	CH_2Cl_2	60	**3a**	0
4	PhC≡CH	10	–[c]	60	**3a**	87
5	PhC≡CPh	10	–	60	**3b**	43
6	EtC≡CEt	10	–	60	**3c**	44
7	HC≡CC_6H_{13}	10	–	60	**3d**	48
8	PhC≡CH	1	–	60	**3a**	trace
9	PhC≡CH	5	–	60	**3a**	<10
10	PhC≡CH	10	–	50	**3a**	66
11	PhC≡CH	10	–	70	**3a**	69
12	PhC≡CH	10	–	80	**3a**	65

[a] Reaction conditions: **1′** (3 mmol), **2a** (4.5 mmol), solvent (4 mL). [b] Isolated yield after reduction by $LiAlH_4$. [c] Under solvent-free conditions.

As shown in Table 2, the yield of the reaction depends on the solvent used. THF (Table 2, entry 1) and toluene (Table 1, entry 2) are feasible solvents, whereas little or no **3a** was obtained with CH_3CN or CH_2Cl_2 (Table 2, entries 2 and 3). However, solvent-free conditions are most suitable for the reaction (Table 2, entry 4) as the yield of **3a** was 87%. Next, the reactivities of a variety of alkynes (diphenylacetylene, 3-hexyne, 1-octyne) catalyzed by 10 mol-% $GaCl_3$ at 60 °C under solvent-free conditions were investigated. We

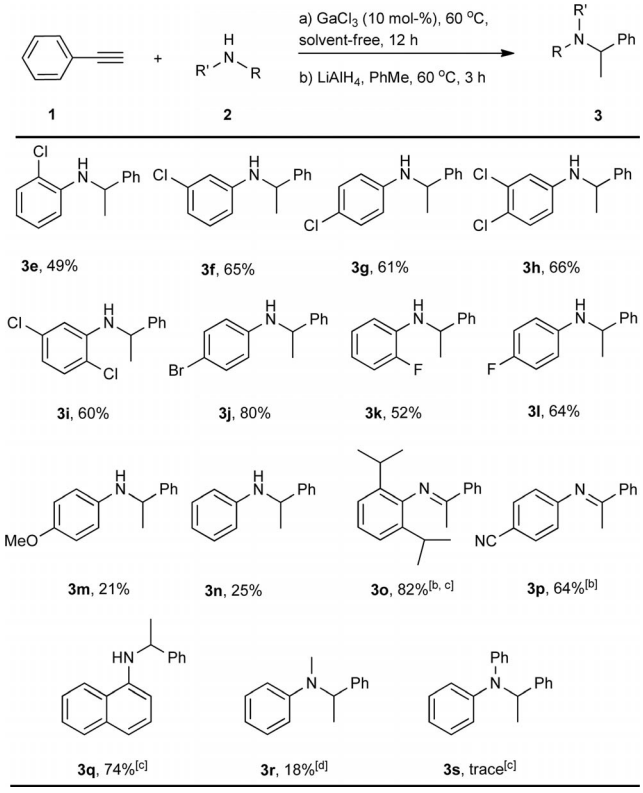
found that aliphatic alkynes are not as reactive as arylalkynes; this is evident from the reactions of 3-hexyne (Table 2, entry 6) and 1-octyne (Table 2, entry 7) with 2,4-dichloroaniline (**2a**), which gave yields of 44 and 48% of 2,4-dichloro-*N*-(3-hexyl)aniline (**3c**) and 2,4-dichloro-*N*-(2-octyl)aniline (**3d**), respectively, as compared with an 87% yield for the reaction of phenylacetylene (**1**) with **2a** under the same conditions. Diphenylacetylene gave a 43% yield, presumably due to the steric hindrance of the bulky phenyl group (Table 2, entry 5). Thus, phenylacetylene (**1**) is a suitable substrate for the hydroamination reaction. Catalyst loading is very important to the yield of the reaction. A 5 mol-% catalyst loading at 60 °C gave a yield of less than 10% of **3a** after 12 h (Table 2, entry 9); on further reducing the catalyst loading to 1 mol-% (Table 2, entry 8), only a trace amount of the product was observed, as determined by GC–MS, and could not be isolated. The temperature of the reaction did not dramatically influence the yield of **3a**. As the temperature was reduced to 50 °C, the product **3a** was obtained in 66% yield under solvent-free conditions with a catalyst loading of 10 mol-% (Table 2, entry 10); yields of 69 and 65% were obtained at 70 (Table 2, entry 11) and 80 °C (Table 2, entry 12), respectively.

Gallium Trichloride Catalyzed Hydroamination of Phenylacetylene (1) with Aromatic Amines

With the optimized reaction conditions in hand, we further investigated the scope of the reaction by screening a larger selection of amines. The results are given in Table 3.

As we can see in Table 3, the $GaCl_3$-catalyzed hydroamination of phenylacetylene (**1**) has been achieved with both primary and secondary aromatic amines. For the primary aromatic amines, hydroamination products containing different functionalities, including halogens (**3e**–**3l**), methoxy (**3m**), isopropyl (**3o**), and nitrile (**3p**), were formed in moderate-to-excellent yields. In most cases, the Markovnikov products were obtained exclusively (**3e**–**3n**, **3p**, **3r**). The anti-Markovnikov products were occasionally formed, but the Markovnikov product was favored, often in an excess of 91:9, over the anti-Markovnikov product (**2o**, **2q**, and **2s**). Steric effects in the primary aromatic amines tested did not have any significant impact on the reaction. For example, 2,6-diisopropylamine (**2o**) and naphthalen-1-amine (**2q**) hydroaminated phenylacetylene in high yields. Secondary aromatic amines gave lower yields than the primary aromatic amines. The hydroamination of phenylacetylene (**1**) with *N*-methylaniline (**2r**) proceeded in 18% yield, whereas only a trace amount of the hydroamination product was observed with diphenylamine (**2s**). The $GaCl_3$-catalyzed hydroamination reactions of phenylacetylene (**1**) with tertiary butylamine, benzylamine, and *p*-toluenesulfonamide were also examined but no hydroamination products were detected. It is evident that the acidities of the amines affect their reactivities. Amines with high pK_a values [*t*BuNH$_2$, pK_a(H$_2$O) = 10.69; BnNH$_2$, pK_a(H$_2$O) = 9.34; TsNH$_2$, pK_a(H$_2$O) = 10.17] do not react, *N*-methylaniline with a pK_a(H$_2$O) of 4.85 gave a yield of 18%, and still lower pK_a(H$_2$O) values, 3.52 (3-chloroaniline), 3.58 (4-fluoroaniline), and 3.53 (4-bromoaniline), gave higher yields of 65, 64, and 80%, respectively.

Table 3. Hydroamination of phenylacetylene (**1**) with various amines **2** under the optimized conditions.[a]

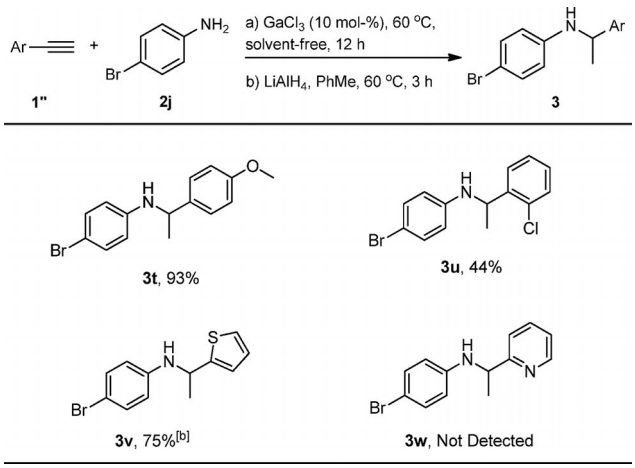


[a] Reaction conditions: **1** (3 mmol), **2** (4.5 mmol), $GaCl_3$ (10 mol-%). Yields of the isolated products are reported. [b] The products were isolated as imines. [c] Trace amounts of anti-Markovnikov products were detected for **2o**, **2q**, and **2s** by GC–MS [Markovnikov/anti-Markovnikov = 98:2 (**2o**), 91:9 (**2q**), 86:14 (**2s**)]. [d] A quinoline derivative was isolated as the main product (see the Supporting Information).

Encouraged by the successful demonstration that 4-bromoaniline (**2j**) is a highly effective nitrogen source and hydroaminates phenylacetylene (**1**) with excellent yield and high regioselectivity, we sought to expand the scope of the reaction by using functionalized phenylacetylenes and heteroarylalkynes. Accordingly, (4-methoxyphenyl)acetylene (**1′′t**), 2-chlorophenylacetylene (**1′′u**), 2-ethynylthiophene (**1′′v**), and 2-ethynylpyridine (**1′′w**) were subjected to the hydroamination reaction with **2j** (Table 4). With an electron-donating OMe substituent at the *para* position, alkyne **1′′t** gave an excellent yield of **3t** with exclusive Markovnikov regioselectivity. The electron-deficient alkyne **1′′u** with a chloro group at the *ortho* position was not a satisfactory substrate for this transformation, affording the corresponding hydroamination product **3u** in moderate yield. Heteroarylalkyne **1′′v** was found to be efficiently hydroaminated by **2j**, affording the desired product **3v** in good yield. However, heteroarylalkyne **1′′w** was not a good sub-

strate for the reaction; the expected hydroamination product **3w** was not detected.

Table 4. Hydroamination of arylacetylenes **1′′** with 4-bromoaniline (**2j**) under the optimized conditions.[a]



[a] Reaction conditions: **1′′** (3 mmol), **2j** (4.5 mmol), $GaCl_3$ (10 mol-%). Yields are reported for the isolated products. [b] A trace amount of the anti-Markovnikov product was determined by GC–MS (Markovnikov/anti-Markovnikov = 90:10).

The high regioselectivity of the hydroamination reaction and low reactivities of the secondary aromatic amines and alkylamines prompted us to study the mechanism of the reactions.

Mechanistic Considerations

To gain a better understanding of this hydroamination process, the detailed mechanism[20] was studied computationally by DFT.[21,22] The calculated potential energy surface of the $GaCl_3$-catalyzed hydroamination reaction of phenylacetylene (**1**) by 4-chloroaniline (**2g**) is shown in Figure 1. The geometric structures of selected transition states and intermediates are presented in Figure 2.

As shown in Figure 1, the reaction starts with the coordination of phenylacetylene (**1**) to the $GaCl_3$ catalyst to give the π complex **IN-1** with a free energy lower than the starting substrates by 1.2 kcal/mol. In complex **IN-1**, the C≡C triple bond is highly asymmetrically bonded to the Ga center with Ga–C distances of 2.248 and 2.788 Å (Figure 2). For the following C–N bond-formation process, both inner-[23] and outer-sphere pathways[24] have been suggested. Our computational results indicate that the energy barrier of the outer-sphere C–N bond-formation process via **TS1b** is higher by about 2.4 kcal/mol than that of the inner-sphere C–N bond-formation process via **TS1a**. Comparison of the geometric structures of **TS1a** and **TS1b** shows that the greater rearrangement of the alkyne moiety in **TS1b** (∠ C1–C2–C3 149.2°) than in **TS1a** (∠ C1–C2–C3 167.5°) may account for the preference for the inner-sphere C–N bond-forming pathway (Figure 2). The zwitterionic intermediate **6** generated from **IN-1** and **2g** via **TS1a** is slightly endergonic by 1.4 kcal/mol. The subsequent intramolecular proton-transfer step from **6** is kinetically unfavorable with an activation energy barrier of 37.9 kcal/mol

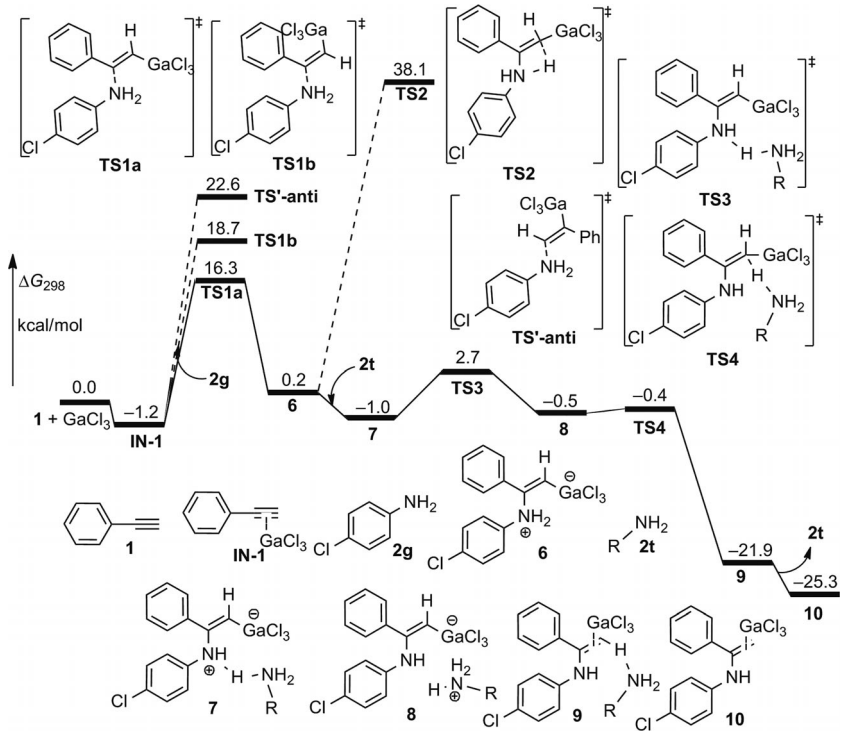


Figure 1. Potential energy surface for the $GaCl_3$-catalyzed hydroamination reaction of phenylacetylene (**1**) by 4-chloroaniline (**2g**) (R = vinyl).

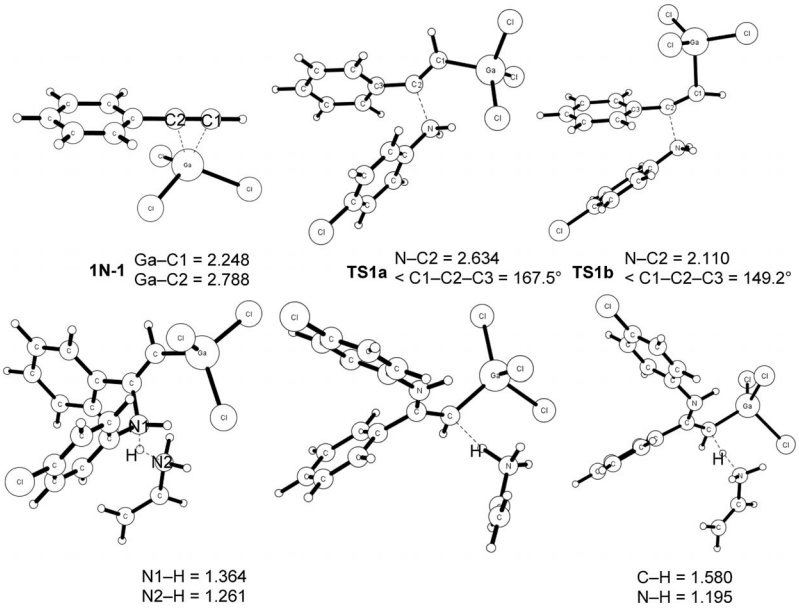


Figure 2. Geometric structures of the selected intermediates and transition states of the $GaCl_3$-catalyzed hydroamination reaction of phenylacetylene (**1**) by aniline **2g**. Selected distances and angles are given in angstroms and degrees.

via transition state **TS2** (Figure 1). Several recent studies have revealed that ligand and solvent could act as proton shuttle to facilitate the hydrogen-migration process.[25] We hypothesize that the Cl ligand of the $GaCl_3$ catalyst or 4-chloroaniline may serve as the proton shuttle in these reactions. According to Figure 1, the proton-transfer step can be realized easily with the assistance of 4-chloroaniline in a stepwise fashion.[26] Here, to save computational cost, a second molecule of 4-chloroaniline (**2g**) was modeled by the amine **2t**. The formation of the hydrogen-bonding intermediate **7** from **6** and **2t** is slightly exergonic by 1.2 kcal/mol. The transition state **TS3** corresponding to the hydrogen-abstraction process from the N1 atom to the N2 atom is 3.7 kcal/mol above the intermediate **7**. The reaction via this transition state leads to the formation of the zwitterionic intermediate **8**, which is only 0.5 kcal/mol less stable than **7**. The subsequent hydrogen-donation process from **8** via **TS4** is quite facile with an activation barrier of 0.1 kcal/mol. Finally, the hydroamination product **10** can be generated from **9** with the loss of a molecule of **2t**. Other possible mechanisms starting with amine activation by the catalyst have recently been proposed for the Lewis acid catalyzed intermolecular olefin hydroamination.[14] We also considered these mechanisms for the title reaction, but the energy barriers were found to be high, ruling out these possibilities.[22]

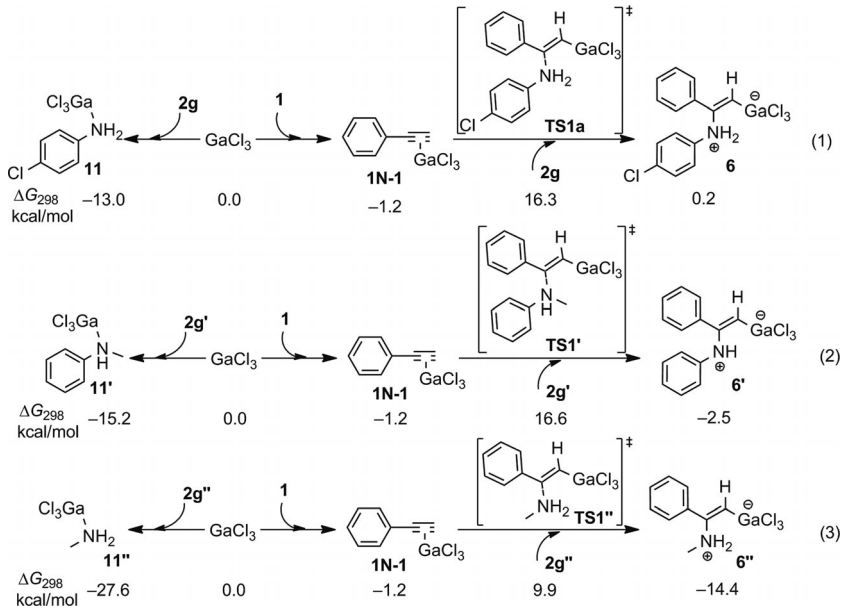
The potential energy surface for the formation of anti-Markovnikov products was also calculated. The free energy of the transition state **TS′-anti** leading to the formation of the anti-Markovnikov products is 22.6 kcal/mol (Figure 1), which is 6.3 kcal/mol higher than that of **TS1a**, which accounts for the exclusive Markovnikov selectivities of the reactions.

The efficiency of the hydroamination reaction is highly amine-dependent. For the hydroamination of phenylacetylene (**1**), the yield was found to increase in the order alkylamine < secondary aromatic amine < primary aromatic amine. As mentioned above, the crucial step that affects the efficiency is expected to be the C–N bond-forming process. Therefore we studied this step for these substrates in detail to gain an understanding of the factors that affect the efficiency of the reaction.

As shown in Scheme 1, for the secondary aromatic amine **2g′** and alkylamine **2g′′**, the free energies of the C–N bond-formation process via transition states **TS1′** and **TS1′′** are 16.6 and 9.9 kcal/mol, that is, equal to or smaller than that of **TS1a**, which indicates that this step is little influenced by steric factors. The main reason for the trend in the experimental observations is that the initial amine/phenylacetylene substitution step is more accessible for the less electron-donating amine.

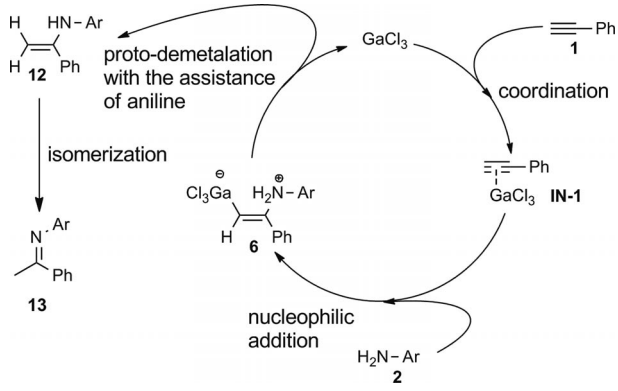
For the alkylamine **2g′′**, the coordination of **2g′′** to $GaCl_3$ to give the σ complex **11′′** is exergonic by 27.6 kcal/mol, and thus the energy barrier for the C–N bond-forming process is 37.5 kcal/mol. For the primary aromatic amine **2g** and secondary aromatic amine **2g′**, the formation of the σ complexes **11** and **11′** is exergonic by 13.0 and 15.2 kcal/mol, and thus the energy barriers for the C–N bond-forming process are 29.3 and 31.8 kcal/mol, respectively. Thus, the low reactivities of the alkylamines are well explained by the higher energy barriers of the C–N bond-forming process of these amines.

On the basis of previous work[14,18] and our computational results, we propose the reaction mechanism for the $GaCl_3$-catalyzed hydroamination of alkynes shown in Scheme 2. Coordination of phenylacetylene (**1**) to the $GaCl_3$ catalyst produces the intermediate **IN-1**. The subsequent nucleophilic addition of aniline **2** to the intermediate **IN-1** by an inner-sphere pathway gives the zwitterionic intermediate **6**, which can lead to the enamine intermediate



Scheme 1. Energies for the C–N bond-formation processes of the amines **2g**, **2g′**, and **2g′′**.

12 and regenerate the active catalyst $GaCl_3$ through aniline-assisted proton-transfer processes. Finally, the enamine intermediate **12** isomerizes to the final product ketimine **13**.



Scheme 2. Proposed mechanism for the $GaCl_3$-catalyzed hydroamination reaction of phenylacetylene (**1**).

Conclusions

$GaCl_3$ has been identified as an effective catalyst for the hydroamination of phenylacetylene with aromatic amines, predominantly giving the Markovnikov hydroamination products. A plausible mechanism has been proposed based on DFT studies. This mechanism involves the coordination of alkynes to $GaCl_3$, the subsequent nucleophilic attack of amines to the coordination π complex to generate zwitterionic intermediates, and the final aniline-assisted proton-transfer process to produce the Markovnikov products. The proposed mechanism accounts for the Markovnikov selectivity of the reactions and the different reactivities of the amine.

Experimental Section

General: All reactions were carried out in pressure tubes (35 mL, 150 psi) equipped with a magnetic stirring bar and capped with a solid PTFE plug. $GaCl_3$ was purchased from commercial suppliers and used without further purification. Amines were distilled from CaH_2. Alkynes were stored over molecular sieves (4 Å). A Varian Unity Plus 400 MHz (or 300 MHz) spectrometer was used to record ^1H and ^{13}C NMR spectra. GC–MS was performed with a GC–MS-QP2010 instrument using dodecane as internal standard and MS spectra were obtained by TOF-MS.

General Procedure for the Hydroamination Reaction: $GaCl_3$ (0.0528 g, 0.3 mmol), aniline (4.5 mmol), and phenylacetylene (0.306 g, 3 mmol) were added to a 35 mL pressure tube in a drybox. A stirring bar was added to the pressure tube, which was then fitted with a Teflon™ stopper and removed from the drybox. The tube was heated with stirring at 60 °C for 12 h. Then at 0 °C, the reaction solution was carefully added to a suspension of $LiAlH_4$ (0.171 g, 4.5 mmol) in toluene (2 mL) and the mixture was heated with stirring at 60 °C for 3 h. After cooling the solution to 0 °C, the excess $LiAlH_4$ was hydrolyzed with iced water and the precipitate was dissolved by the dropwise addition of an aqueous NaOH solution (2.0 mol L^{-1}). The mixture was then extracted with CH_2Cl_2 (3× 20 mL) and the combined organic layers were dried with $MgSO_4$ and concentrated under vacuum. Column chromatography of the residue on silica gel gave a pure product.

2,4-Dichloro-*N*-(1-phenylethyl)aniline (3a): Product **3a** (87%) was obtained as a colorless oil by column chromatography with petroleum ether as eluent. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.22 (m, 6 H), 6.94 (dd, J = 8.8, 1.9 Hz, 1 H), 6.34 (d, J = 8.8 Hz, 1 H), 4.70 (s, 1 H), 4.51 (m, J = 6.3 Hz, 1 H), 1.59 (d, J = 10.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 144.1, 131.2, 130.9, 130.0, 129.6, 128.0, 123.5, 121.5, 115.5, 55.8, 27.5 ppm. HRMS: calcd. for $C_{14}H_{13}Cl_2N$ 265.0425; found 265.0430.

2,4-Dichloro-*N*-(1,2-diphenylethyl)aniline (3b): Product **3b** (43%) was obtained as a light-green oil by column chromatography with petroleum ether as eluent. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31–

7.27 (m, 3 H), 7.24 (d, J = 6.2 Hz, 5 H), 7.17 (d, J = 2.3 Hz, 1 H), 7.11 (d, J = 6.6 Hz, 2 H), 6.85 (dd, J = 8.8, 2.4 Hz, 1 H), 6.23 (d, J = 8.7 Hz, 1 H), 4.81 (s, 1 H), 4.54 (m, 1 H), 3.17 (dd, J = 13.9, 5.8 Hz, 1 H), 3.05 (dd, J = 13.8, 8.0 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.7, 142.2, 137.5, 129.8, 129.2, 129.0, 128.9, 127.9, 127.4, 126.7, 121.8, 120.1, 113.7, 59.8, 45.7 ppm. HRMS: calcd. for $C_{20}H_{17}Cl_2N$ 341.0738; found 341.0735.

2,4-Dichloro-*N*-(3-hexyl)aniline (3c): Product **3c** (44%) was obtained as a colorless oil by column chromatography with petroleum ether as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 2.3 Hz, 1 H), 7.06 (dd, J = 8.8, 2.3 Hz, 1 H), 6.54 (d, J = 8.8 Hz, 1 H), 4.07 (s, 1 H), 3.30 (d, J = 7.3 Hz, 1 H), 1.67–1.24 (m, 5 H), 0.92 (t, J = 7.3 Hz, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.1, 129.1, 128.0, 120.4, 119.4, 112.3, 54.5, 36.9, 27.6, 19.5, 14.6, 10.4 ppm. HRMS: calcd. for $C_{12}H_{17}Cl_2N$ 245.0738; found 245.0737.

2,4-Dichloro-*N*-(2-octyl)aniline (3d): Product **3d** (48%) was obtained as a colorless oil by column chromatography with petroleum ether as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, J = 2.4 Hz, 1 H), 7.07 (dd, J = 8.8, 2.3 Hz, 1 H), 6.54 (d, J = 8.8 Hz, 1 H), 4.08 (d, J = 7.8 Hz, 1 H), 3.50–3.36 (m, 1 H), 1.64–1.23 (m, 10 H), 1.19 (d, J = 6.3 Hz, 3 H), 0.88 (t, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.6, 129.2, 128.0, 120.6, 119.6, 112.4, 49.0, 37.3, 32.2, 29.7, 26.4, 23.0, 21.0, 14.5 ppm. HRMS: calcd. for $C_{14}H_{21}Cl_2N$ 273.1051; found 273.1052.

2-Chloro-*N*-(1-phenylethyl)aniline (3e): Product **3e** (49%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (30:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 4 H), 7.23 (s, 1 H), 6.95 (t, J = 7.8 Hz, 1 H), 6.56 (t, J = 7.6 Hz, 1 H), 6.39 (d, J = 8.1 Hz, 1 H), 4.68 (s, 1 H), 4.52 (dd, J = 12.4, 6.3 Hz, 1 H), 1.57 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.6, 143.0, 129.0, 128.7, 127.6, 127.0, 125.7, 118.9, 117.2, 112.5, 53.4, 25.2 ppm. HRMS: calcd. for $C_{14}H_{14}ClN$ 231.0815; found 231.0815.

3-Chloro-*N*-(1-phenylethyl)aniline (3f): Product **3f** (65%) was obtained as a yellow oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 4 H), 7.22 (dd, J = 7.1, 5.1 Hz, 1 H), 6.96 (t, J = 8.1 Hz, 1 H), 6.59 (d, J = 7.9 Hz, 1 H), 6.48 (s, 1 H), 6.34 (d, J = 8.2 Hz, 1 H), 4.44 (d, J = 6.1 Hz, 1 H), 4.09 (s, 1 H), 1.48 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 144.4, 134.8, 130.1, 128.7, 127.1, 125.8, 117.2, 113.1, 111.5, 53.4, 24.8 ppm. HRMS: calcd. for $C_{14}H_{14}ClN$ 231.0815; found 231.0809.

4-Chloro-*N*-(1-phenylethyl)aniline (3g): Product **3g** (61%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 3.1 Hz, 4 H), 7.24 (s, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 6.40 (d, J = 8.8 Hz, 2 H), 4.47–4.37 (m, 1 H), 4.04 (s, 1 H), 1.50 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0, 145.0, 129.2, 129.0, 127.3, 126.0, 122.0, 114.7, 53.8, 25.3 ppm. HRMS: calcd. for $C_{14}H_{14}ClN$ 231.0815; found 231.0816.

3,4-Dichloro-*N*-(1-phenylethyl)aniline (3h): Product **3h** (66%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (d, J = 6.0 Hz, 4 H), 7.24 (d, J = 5.5 Hz, 1 H), 7.07 (d, J = 8.7 Hz, 1 H), 6.57 (d, J = 2.7 Hz, 1 H), 6.31 (dd, J = 8.8, 2.6 Hz, 1 H), 4.41 (m, J = 6.7 Hz, 1 H), 4.12 (s, 1 H), 1.50 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.8, 144.2, 132.7, 130.6, 129.0, 127.4, 125.8, 119.8, 114.6, 113.0, 53.6, 25.0 ppm. HRMS: calcd. for $C_{14}H_{13}Cl_2N$ 265.0425; found 265.0433.

2,5-Dichloro-*N*-(1-phenylethyl)aniline (3i): Product **3i** (60%) was obtained as a pale-yellow oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.28 (m, 4 H), 7.26–7.19 (m, 1 H), 7.12 (d, J = 8.4 Hz, 1 H), 6.57–6.48 (m, 1 H), 6.38 (s, 1 H), 4.72 (s, 1 H), 4.46 (m, J = 6.5 Hz, 1 H), 1.54 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.8, 143.8, 133.4, 129.6, 128.9, 127.3, 125.7, 117.1, 117.0, 112.2, 53.3, 24.9 ppm. HRMS: calcd. for $C_{14}H_{13}Cl_2N$ 265.0425; found 265.0419.

4-Bromo-*N*-(1-phenylethyl)aniline (3j): Product **3j** (80%) was obtained as a yellow oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (d, J = 4.8 Hz, 4 H), 7.24–7.19 (m, 1 H), 7.15 (d, J = 8.8 Hz, 2 H), 6.37 (d, J = 8.8 Hz, 2 H), 4.43 (m, J = 6.7 Hz, 1 H), 4.07 (s, 1 H), 1.51 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 144.6, 131.8, 128.7, 127.0, 125.7, 114.9, 108.8, 53.5, 25.0 ppm. HRMS: calcd. for $C_{14}H_{14}BrN$ 275.0310; found 275.0298.

2-Fluoro-*N*-(1-phenylethyl)aniline (3k): Product **3k** (52%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (30:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dt, J = 13.9, 6.8 Hz, 4 H), 7.31–7.20 (m, 1 H), 6.99 (dd, J = 11.8, 8.1 Hz, 1 H), 6.85 (t, J = 7.7 Hz, 1 H), 6.67–6.54 (m, 1 H), 6.47 (t, J = 8.4 Hz, 1 H), 4.61–4.48 (m, 1 H), 4.34 (s, 1 H), 1.58 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 150.4, 145.0, 135.9, 128.9, 127.2, 125.9, 124.6, 116.7, 114.4, 113.4, 53.5, 25.3 ppm. HRMS: calcd. for $C_{14}H_{14}FN$ 215.1110; found 215.1110.

4-Fluoro-*N*-(1-phenylethyl)aniline (3l): Product **3l** (64%) was obtained as a yellow oil after column chromatography with petroleum ether/ethyl acetate (30:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.27 (m, 4 H), 7.23–7.15 (m, 1 H), 6.78 (t, J = 8.7 Hz, 2 H), 6.42 (dd, J = 8.7, 4.4 Hz, 2 H), 4.40 (m, J = 6.7 Hz, 1 H), 3.91 (s, 1 H), 1.49 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.2, 143.8, 128.8, 127.2, 126.0, 115.8, 115.6, 114.2, 54.3, 25.3 ppm. HRMS: calcd. for $C_{14}H_{14}FN$ 215.1110; found 215.1112.

4-Methoxy-*N*-(1-phenylethyl)aniline (3m): Product **3m** (21%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (8:1) as eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.27 (m, 4 H), 7.22 (dd, J = 12.3, 5.1 Hz, 1 H), 6.68 (d, J = 8.7 Hz, 2 H), 6.46 (d, J = 8.8 Hz, 2 H), 4.40 (m, J = 6.5 Hz, 1 H), 3.80 (s, 1 H), 3.68 (s, 3 H), 1.49 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 145.6, 141.7, 128.8, 127.0, 126.0, 114.9, 114.7, 55.9, 54.4, 25.3 ppm. HRMS: calcd. for $C_{15}H_{17}NO$ 227.1310; found 227.1313.

***N*-(1-Phenylethyl)aniline (3n):** Product **3n** (25%) was obtained as a colorless oil after column chromatography with petroleum ether/ethyl acetate (60:1) as eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (dt, J = 14.9, 7.4 Hz, 4 H), 7.19 (dd, J = 11.8, 4.8 Hz, 1 H), 7.07 (t, J = 7.8 Hz, 2 H), 6.63 (t, J = 7.3 Hz, 1 H), 6.49 (d, J = 8.1 Hz, 2 H), 4.46 (q, J = 6.7 Hz, 1 H), 4.06 (d, J = 21.8 Hz, 1 H), 1.49 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.21, 145.17, 129.08, 128.61, 126.84, 125.81, 117.21, 113.27, 53.42, 24.96 ppm. HRMS: calcd. for $C_{14}H_{15}N$ 197.1204; found 197.1205.

2,6-Diisopropyl-*N*-(1-phenylethylidene)aniline (3o): Product **3o** (82%) was obtained as a yellow crystal by recrystallization (methanol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.12–7.96 (m, 2 H), 7.47 (d, J = 3.5 Hz, 3 H), 7.15 (d, J = 6.9 Hz, 2 H), 7.07 (dd, J = 8.5, 6.5 Hz, 1 H), 2.75 (dt, J = 13.7, 6.8 Hz, 2 H), 2.10 (s, 3 H), 1.22–

1.07 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.88, 146.86, 139.23, 136.21, 130.52, 128.54, 127.26, 123.42, 123.06, 28.33, 23.26, 18.25 ppm. HRMS: calcd. for $C_{20}H_{25}N$ 279.1987; found 279.1985.

4-[(1-Phenylethylidene)amino]benzonitrile (3p): Product **3p** (64%) was obtained as a yellow crystal by recrystallization (methanol). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.4 Hz, 2 H), 7.63 (d, J = 8.3 Hz, 2 H), 7.47 (q, J = 6.2 Hz, 3 H), 6.86 (d, J = 8.3 Hz, 2 H), 2.23 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.45, 156.04, 138.65, 133.52, 131.40, 128.76, 127.56, 120.26, 119.61, 106.70, 18.02 ppm. HRMS: calcd. for $C_{15}H_{22}N_2$ 220.1000; found 220.1001.

***N*-(1-Phenylethyl)naphthalen-1-amine (3q):** Product **3q** (74%) was obtained as a white crystal after column chromatography with petroleum ether/ethyl acetate (40:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 4.8 Hz, 1 H), 7.75 (dt, J = 16.3, 7.6 Hz, 1 H), 7.53–7.35 (m, 4 H), 7.29 (t, J = 7.2 Hz, 2 H), 7.24–7.12 (m, 3 H), 6.39 (s, 1 H), 4.74 (s, 1 H), 4.65 (dd, J = 13.1, 6.5 Hz, 1 H), 1.64 (d, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.99, 142.17, 134.36, 128.85, 128.78, 127.05, 126.66, 125.89, 125.72, 124.77, 123.32, 119.87, 117.31, 106.10, 53.62, 25.34 ppm. HRMS: calcd. for $C_{18}H_{17}N$ 247.1361; found 247.1362.

***N*-Methyl-*N*-(1-phenylethyl)aniline (3r):** Product **3r** (18%) was obtained as a colorless liquid after column chromatography with petroleum ether as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.17 (m, 7 H), 6.88 (d, J = 8.2 Hz, 2 H), 6.77 (t, J = 7.2 Hz, 1 H), 5.17 (q, J = 6.8 Hz, 1 H), 2.71 (s, 3 H), 1.59 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.49, 143.09, 129.50, 128.67, 127.19, 127.11, 116.93, 113.33, 56.78, 32.14, 16.61 ppm. HRMS: calcd. for $C_{15}H_{17}N$ 211.1361; found 211.1363.

4-Bromo-*N*-[1-(4-methoxyphenyl)ethyl]aniline (3t): Product **3t** (93%) was obtained as a yellow oil after column chromatography with petroleum ether/ethyl acetate (10:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.10 (m, 4 H), 6.89 (dd, J = 6.3, 2.2 Hz, 2 H), 6.41 (dd, J = 6.6, 2.1 Hz, 2 H), 4.42 (s, 1 H), 4.07 (s, 1 H), 3.81 (s, 3 H), 1.52 (d, J = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.84, 141.52, 131.89, 127.02, 122.09, 110.18, 109.35, 104.03, 50.53, 48.13, 20.27 ppm. HRMS: calcd. for $C_{15}H_{16}BrNO$ 305.0415; found 306.0476(M + 1).

4-Bromo-*N*-[1-(2-chlorophenyl)ethyl]aniline (3u): Product **3u** (44%) was obtained as a light-yellow oil after column chromatography with petroleum ether/ethyl acetate (15:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, J = 2.7 Hz, 2 H), 7.26–7.07 (m, 4 H), 6.29 (dd, J = 6.5, 2.0 Hz, 2 H), 4.90–4.74 (m, 1 H), 4.11 (d, J = 6.6 Hz, 1 H), 1.47 (d, J = 6.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.92, 136.67, 127.75, 127.11, 125.07, 123.48, 122.69, 121.84, 110.03, 104.38, 45.57, 18.17 ppm. HRMS: calcd. for $C_{14}H_{13}BrClN$ 308.9920; found 309.9987 $[M + 1]^+$.

4-Bromo-*N*-[1-(2-thienyl)ethyl]aniline (3v): Product **3v** (75%) was obtained as a light-yellow oil after column chromatography with petroleum ether/ethyl acetate (25:1) as eluent. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.08 (m, 3 H), 6.91 (d, J = 4.2 Hz, 2 H), 6.45 (dd, J = 6.3, 2.3 Hz, 2 H), 4.85–4.64 (m, 1 H), 3.98 (s, 1 H), 1.57 (d, J = 6.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.87, 141.19, 127.18, 122.14, 119.11, 118.50, 110.42, 104.73, 44.83, 20.05 ppm. HRMS: calcd. for $C_{12}H_{12}BrNS$ 280.9874; found 281.9928, (M + 1).

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures for the hydroamination reaction, spectroscopic data and computational details.

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[26] The energy barrier for Cl-assisted pathway was found to be higher than that for the aniline-assisted pathway, see the Supporting Information for details.

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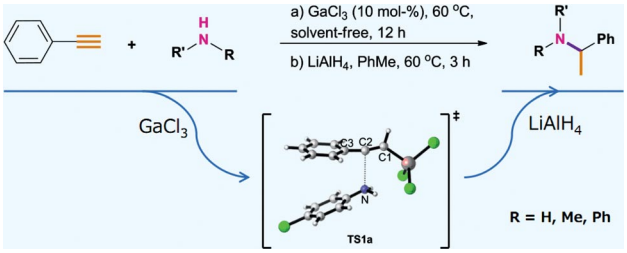
Hydroamination of Alkynes



The hydroamination of alkynes with aromatic amines catalyzed by gallium trichloride is presented. Markovnikov products were exclusively obtained with most of the aniline derivatives. The reaction mechanism was investigated by DFT calculations. The regioselectivities of the reactions as well as the reactivities of the different amine substrates are well explained by the proposed mechanism.

Keywords: Synthetic methods / Hydroamination / Gallium / Alkynes / Reaction mechanisms / Density functional calculations

