Ruthenium-Catalyzed Propargylic Substitution Reactions of Propargylic Alcohols with Oxygen-, Nitrogen-, and Phosphorus-Centered Nucleophiles

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Abstract: The scope and limitations of the ruthenium-catalyzed propargylic substitution reaction of propargylic alcohols with heteroatom-centered nucleophiles are presented. Oxygen-, nitrogen-, and phosphorus-centered nucleophiles such as alcohols, amines, amides, and phosphine oxide are available for this catalytic reaction. Only the thiolate-bridged diruthenium complexes can work as catalysts for this reaction. Results of some stoichiometric and catalytic reactions indicate that the catalytic propargylic substitution reaction proceeds via an allenylidene complex formed in situ, whereby the attack of nucleophiles to the allenylidene C_γ atom is a key step. Investigation of the relative rate constants for the reaction of propargylic alcohols with several *para*-substituted anilines reveals that the attack of anilines on the allenylidene C_γ atom is not involved in the rate-determining step and rather the acidity of conjugated anilines of an alkynyl complex, which is formed after the attack of aniline on the C_γ atom, is considered to be the most important factor to determine the rate of this catalytic reaction. The key point to promote this catalytic reaction by using the thiolate-bridged diruthenium complexes is considered to be the ease of the ligand exchange step between a vinylidene ligand on the diruthenium complexes and another propargylic alcohol in the catalytic cycle. The reason why only the thiolate-bridged diruthenium complexes promote the ligand exchange step more easily with respect to other monoruthenium complexes in this catalytic reaction should be that one Ru moiety, which is not involved in the allenylidene formation, works as an electron pool or a mobile ligand to another Ru site. The catalytic procedure presented here provides a versatile, direct, and one-step method for propargylic substitution of propargylic alcohols in contrast to the so far well-known stoichiometric and stepwise Nicholas reaction.

Keywords: alcohols · amines · nucleophilic subsitution · propargylic alcohols · ruthenium

Introduction

Allylic substitution reactions of allylic alcohol derivatives with nucleophiles catalyzed by transition-metal complexes are one of the most successful and reliable methods in organic synthesis.[1] The process is catalyzed by various transition-metal complexes derived from nickel, palladium, platinum, cobalt, rhodium, iridium, iron, ruthenium, molybdenum, and tungsten.[1] A variety of nucleophiles such as alcohols, amines, thiols, and active methine and methylene compounds are available for this reaction, which proceeds via (η-allyl)metal species to afford a wide variety of allylated products with high chemo-, regio-, and stereoselectivities.[1]

In sharp contrast, much less attention has been paid to the propargylic substitution reactions of propargylic alcohol derivatives with nucleophiles. The Nicholas reaction has so far been known to be an effective tool for propargylic substitution reaction.[2] In addition to heteroatom-centered nucleophiles, such as alcohols, amines, and thiols, a wide varie-

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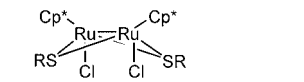
ty of carbon-centered nucleophiles, including simple ketones such as acetone, are also available for the Nicholas reaction.[2,3] This reaction, however, has some drawbacks: a stoichiometric amount of $[Co_2(CO)_8]$ is required, and several steps are necessary to obtain propargylic-substituted products from propargylic alcohols via cationic propargyl complexes $[Co_2(CO)_6(propargyl)]^+$.[2,3] On the other hand, several catalytic propargylic substitution reactions have been recently reported, in which some transition-metal complexes, such as copper, titanium, iridium, ruthenium, rhenium, and palladium complexes, worked as effective catalysts to give the corresponding propargylic compounds from propargylic alcohols or their derivatives.[4] The kind of available nucleophiles, however, depends a lot on the nature of transition-metal complexes. To the best of our knowledge, no general method for catalytic propargylic substitution reactions has so far been reported.

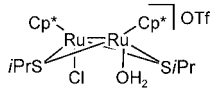
Since the first discovery of the allenylidene complex in 1976, transition-metal allenylidene (M=C=C=C<) complexes have attracted a great deal of attention as a new type of organometallic intermediate.[5] In fact, cationic transition-metal allenylidene complexes $[M^+=C=C=CR^1R^2]$, readily available by dehydration of propargylic alcohols coordinated to an unsaturated metal center, can be regarded as stabilized propargylic cations because of the extensive contribution of the metal–alkynyl resonance form $[M-C\equiv CC^+R^1R^2]$.[6] Theoretical studies also indicate that the C_α and C_γ atoms of allenylidene ligands are electrophilic centers, while the C_β atom behaves as a nucleophilic site.[7] In fact, *stoichiometric* reactions of allenylidene ruthenium complexes with a variety of nucleophiles have been reported, in which nucleophiles attack either the allenylidene C_α or C_γ atom to afford Fischer-type carbenes or alkynyl complexes, respectively.[7]

It is now known that nucleophilic addition at C_γ occurs regioselectively when electron-rich and/or bulky metallic fragments are used, leading to a large variety of σ-alkynyl complexes $[M-C\equiv CC(Nu)R^1R^2]$.[7] Especially, Gimeno and coworkers have developed an interesting synthetic procedure for the propargylic substitution reaction of 2-propyn-1-ols mediated by the metallic complex $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$.[8] Here, allenylidene complexes are formed in the first step and they are subsequently transformed into the corresponding σ-alkynyl derivatives, which undergo a selective protonation to afford the vinylidene complexes. Finally, demetalation from the vinylidene complexes with acetonitrile leads to the functionalized terminal alkynes in high yields. This synthetic methodology is considered to be an alternative to the Nicholas reaction[2] (vide supra), although a stoichiometric amount of ruthenium complex is required and also several steps are necessary to obtain propargylic-substituted products from propargylic alcohols. In addition, quite recently, some unprecedented reactivities of allenylidene complexes have been reported, but all of them are limited to stoichiometric reactions.[9] In fact, only a few examples of *catalytic* reactions via allenylidene intermediates have been reported until now.[10]

We have long been interested in the development of homogeneous catalysis of polynuclear transition-metal complexes, since direct and indirect cooperation of several transition metals can be expected for the activation of substrates to provide novel transformations that are not attainable at a conventional monometallic center.[11] Toward this end, our studies have been focused on the synthesis and reactivity of polynuclear noble-metal complexes with bridging sulfur ligands.[12] In the course of our investigation, we have so far synthesized a series of thiolate-bridged diruthenium complexes, such as $[(Cp^*)Ru(\mu_2\text{-}S\textit{i}Pr)_2Ru(Cp^*)]$ (Ru^{II}–Ru^{II}) ($Cp^* = \eta^5\text{-}C_5Me_5$) and $[(Cp^*)Ru(\mu_2\text{-}S\textit{i}Pr)_3Ru(Cp^*)]$ (Ru^{II}–Ru^{III}), and disclosed that these complexes provide unique reaction sites for various *stoichiometric* transformations of terminal alkynes.[13] During our further study on this subject using the thiolate-bridged diruthenium complexes $[(Cp^*)RuCl(\mu_2\text{-}SR)_2Ru(Cp^*)Cl]$ (Ru^{III}–Ru^{III}) (R = Me (**1a**), Et (**1b**), *n*Pr (**1c**), *i*Pr (**1d**)), and $[(Cp^*)RuCl(\mu_2\text{-}S\textit{i}Pr)_2Ru(Cp^*)(OH_2)]OTf$ (Ru^{III}–Ru^{III}) (**1e**; $OTf = OSO_2CF_3$),[14] we eventually found that these complexes work as good catalysts for propargylic substitution reaction of propargylic alcohols bearing a terminal alkyne with a variety of nucleophiles.[15] Not only heteroatom-centered but also carbon-centered nucleophiles could be employed for this catalytic propargylic substitution reaction, which proceeded via an allenylidene ruthenium complex as a key intermediate. Here, we describe the scope and limitations of catalytic propargylic substitution reaction of propargylic alcohols with heteroatom-centered nucleophiles such as alcohols, amines, amides, and diphenylphosphine oxide in detail together with unambiguous X-ray structural determination of an intermediate allenylidene complex. In addition, some mechanistic consideration on the reaction pathway, including the results of stoichiometric reactions of allenylidene intermediates with nucleophiles, are presented in this article. Results of the catalytic reaction of propargylic alcohols with thiols[16] and carbon-centered nucleophiles including simple ketones, such as acetone,[17] and 1,3-dicarbonyl compounds, such as 1,3-cyclohexanedione,[18] have been reported separately.



R = Me (**1a**), Et (**1b**), *n*Pr (**1c**), *i*Pr (**1d**)

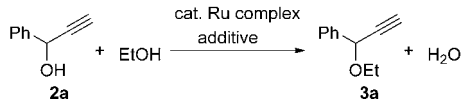


1e

Results and Discussion

Propargylic substitution reaction with oxygen-centered nucleophiles: At first, the propargylic substitution reaction of propargylic alcohols with various alcohols was investigated to obtain the corresponding ethers. A variety of thiolate-bridged diruthenium complexes and monoruthenium complexes were examined as catalysts in the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with EtOH. Typical results are shown in Table 1. Interestingly, only the thiolate-bridged di-

Table 1. Propargylic substitution reaction of propargylic alcohol **2a** with EtOH.[a]



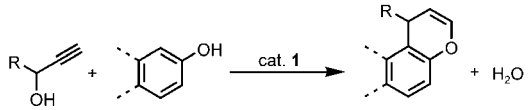
	Ruthenium catalyst (mol %)[b]	Additive (mol %)[b]	Conditions T [°C]/t [min]	GLC yield [%]
1	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (5)	–	60/15	85
2	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (5)	NH_4BF_4 (10)	60/15	95 (88)[c]
3	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (1)	NH_4BF_4 (10)	60/15	32
4	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (5)	NH_4BF_4 (10)	25/60	90
5	–[d]	NH_4BF_4 (10)	60/15	0
6	$[(Cp^*)RuCl(SEt)]_2$ (**1b**) (5)	–	60/15	81
7	$[(Cp^*)RuCl(SnPr)]_2$ (**1c**) (5)	–	60/15	83
8	$[(Cp^*)RuCl(SiPr)]_2$ (**1d**) (5)	–	60/15	78
9	$[(Cp^*)RuCl(SiPr)_2Ru(Cp^*)Cl]OTf$ (**1e**) (5)	–	60/15	69
10	$[(Cp^*)Ru(SiPr)_3Ru(Cp^*)]$ (**1f**) (5)	–	60/15	1
11	$[(Cp^*)Ru(SiPr)_2Ru(Cp^*)]$ (**1g**) (5)	–	60/15	0
12	$[(Cp^*)RuCl(PPh_3)_2]$ (5)	NH_4BF_4 (10)	60/15	1
13	$[CpRuCl(PPh_3)_2]$ (5)	NH_4BF_4 (10)	60/15	1
14	$[RuCl_2(dppe)_2]$ (5)	NH_4BF_4 (10)	60/15	1
15	$[RuCl_2(PPh_3)_3]$ (5)	NH_4BF_4 (10)	60/15	1
16	$[\{RuCl_2(p\text{-cymene})\}_2]$ (5)	NH_4BF_4 (10)	60/15	1
17	$[(C_9H_7)RuCl(PPh_3)_2]$ (5)	NH_4BF_4 (10)	60/15	1
18	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (5)	NH_4BF_4 (10)	60/15	(84)[c,e]
19	$[(Cp^*)RuCl(SMe)]_2$ (**1a**) (5)	NH_4BF_4 (10)	60/15	(91)[c,f]

[a] All the reactions of **2a** (0.20 mmol) with EtOH (5 mL) were carried out in the presence of catalyst. [b] Mol % to **2a**. [c] Isolated yield. [d] In the absence of catalyst. [e] MeOH was used in place of EtOH. Yield of **3b**. [f] *i*PrOH was used in place of EtOH. Yield of **3c**.

ruthenium complexes worked effectively. In fact, in the presence of a catalytic amount of **1a**, the treatment of **2a** in EtOH at 60 °C for 15 min gave the corresponding propargylic ether (**3a**) in 85 % GLC yield with a complete regioselectivity (Table 1, entry 1). The formation of neither an allenic by-product nor another regioisomer of **3a** was observed by GLC and ^{1}H NMR spectroscopy. The addition of NH_4BF_4 improved the catalytic activity (95 % GLC yield: Table 1, entry 2), probably by affording a cationic thiolate-bridged diruthenium complex with a vacant site. The use of 1 mol % of **1a** decreased the yield of **3a** (Table 1, entry 3). The reaction at room temperature was completed within 1 h to give **3a** in 90 % GLC yield (Table 1, entry 4). On the other hand, in the absence of **1a**, no reaction occurred at all (Table 1, entry 5). The kind of bridging thiolato ligands in the diruthenium complex did not have much influence on the catalytic activity. The complex with the sterically demanding S*i*Pr group (**1d**) exhibited a slightly lower catalytic activity, while the complexes with SEt and S*n*Pr groups (**1b** and **1c**, respectively) showed almost the same catalytic activity as **1a** (Table 1, entries 6–8). A cationic thiolate-bridged diruthenium complex (**1e**) also worked as a catalyst for the propargylic etherification (Table 1, entry 9). In sharp contrast to the reactivity of the thiolate-bridged diruthenium(Ru^{III}–Ru^{III}) complexes (**1d** and **1e**), both diruthenium(Ru^{II}–Ru^{III}) and diruthenium(Ru^{II}–Ru^{II}) complexes[13] (**1f** and **1g**) were ineffective (Table 1, entries 10 and 11). It is worth noting that conventional monoruthenium complexes such as $[RuCl(Cp^*)(PPh_3)_2]$, $[RuCl(Cp)(PPh_3)_2]$ ($Cp = \eta^5$-C_5H_5), $[RuCl_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane), $[RuCl_2(PPh_3)_2]$, $[RuCl_2(p\text{-cymene})]_2$, and $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)_2]$, which are known to react with propargylic alcohols to produce the corresponding allenylidene complexes (vide infra),[7] did not work at all as catalysts under the conditions investigated here (Table 1, entries 12–17). The use of AgOTf in place of NH_4BF_4 did not promote the catalytic reactions at all. When MeOH and *i*PrOH were used in place of EtOH, the corresponding methyl and isopropyl ethers (**3b** and **3c**) were obtained in 84 and 91 % yields, respectively (Table 1, entries 18 and 19).

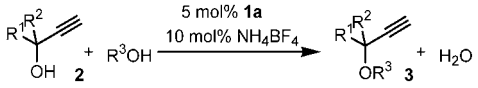
Results of various reactions between propargylic and nucleophilic alcohols catalyzed by **1a** and NH_4BF_4 are shown in Table 2. Propargylic substitution reaction of 1-monoalkyl- and 1,1-dialkyl-substituted propargylic alcohols (**2b**–**2d**) at 60 °C occurred rapidly to afford the corresponding ethers (**3d**–**3f**, respectively) in high yields (Table 2, entries 1–3). In contrast, reactions of 1,1-diaryl-substituted propargylic alcohols (**2e** and **2f**) were sluggish under identical conditions, a prolonged time being required to produce the diaryl-substituted ethers (**3g** and **3h**) in moderate yields (Table 2, entries 4 and 5). In addition to the use of EtOH, MeOH, and *i*PrOH, other types of alcohols bearing a chiral moiety could also be employed for the propargylic substitution reaction as nucleophiles, with 1,2-dichloroethane ($ClCH_2CH_2Cl$) used as the solvent in place of the alcohols. When the reactions of **2a** with five equivalents of chiral alcohols were carried out in $ClCH_2CH_2Cl$ at 60 °C for 1 h, a mixture of two diastereomeric isomers was obtained in moderate to high yields with the isomer ratio of approximately 1:1 (Table 2, entries 6–10). The exact ratios of two diastereomeric isomers are shown in the Experimental Section.

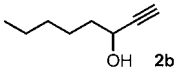
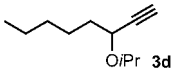
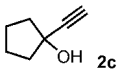
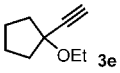
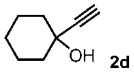
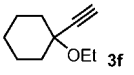
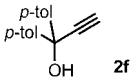
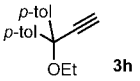
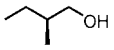
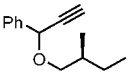
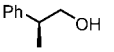
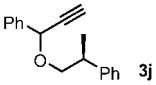
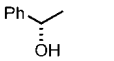
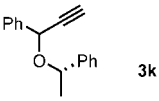
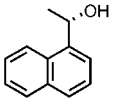
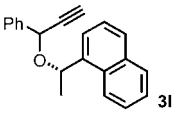
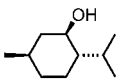
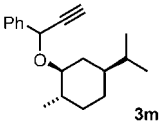
As has been reported,[19] cycloaddition of propargylic alcohols with phenols bearing electron-donating groups proceeded to give the corresponding 4*H*-1-benzopyrans in good yields (Scheme 1). However, propargylation of phenol with **2a** afforded the corresponding phenyl propargylic ether



Scheme 1. Cycloaddition of propargylic alcohols with phenols bearing electron-donating groups.

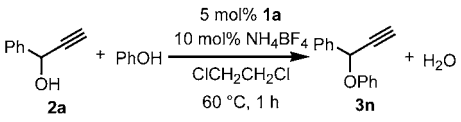
Table 2. Propargylic substitution reactions of propargylic alcohols (**2**) with alcohols catalyzed by **1a**.[a]



	Propargylic alcohol (**2**)	Alcohol	Conditions T [°C]/t [min]	Propargylic ether (**3**)	Yield [%][b]
1	 **2b**	*i*PrOH	60/15	 **3d**	75
2	 **2c**	EtOH	25/30	 **3e**	54
3	 **2d**	EtOH	25/30	 **3f**	57
4	 **2e**	EtOH	60/1200	 **3g**	62
5	 **2f**	EtOH	60/1200	 **3h**	61
6[c]	 **2a**		60/60	 **3i**	80[d]
7[c]	 **2a**		60/60	 **3j**	92[d]
8[c]	 **2a**		60/60	 **3k**	69[d]
9[c]	 **2a**		60/60	 **3l**	64[d]
10[c]	 **2a**		60/60	 **3m**	71[d]

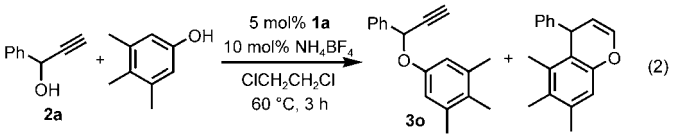
[a] Reactions of propargylic alcohol (**2**; 0.60 mmol) with alcohol (15 mL) were carried out in the presence of **1a** and NH_4BF_4 (entries 1–5). [b] Isolated yield. [c] Reactions of propargylic alcohol (**2**) (0.60 mmol) with alcohol (3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (15 mL) (runs 6–10). [d] The ratio of two diastereomeric isomers is given in the Experimetal Section.

(**3n**) in 65% isolated yield [Eq. (1)], indicating that phenols without electron-donating groups can be propargylated to give the corresponding aryl propargylic ethers. In fact, the

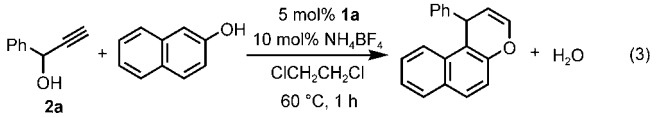


(1)

reaction of **2a** with 3,4,5-trimethylphenol gave a mixture of propargylic ether (**3o**) and 4*H*-1-benzopyran in a 2:1 ratio [Eq. (2)]. When the reaction of **2a** with 2-naphthol was carried out at 60°C for 1 h, 1-phenyl-1*H*-naphtho[2,1-*b*]pyran was isolated in 80% yield [Eq. (3)].[19] Previously, we confirmed that the cycloaddition proceeded via an allenylidene intermediate.[19]



(2)

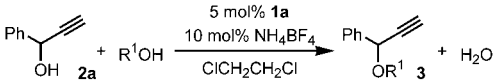


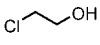
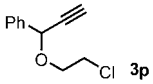
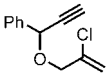
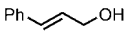
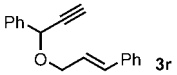
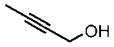
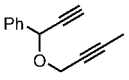
(3)

The Williamson reaction is the well-known and most widely used method for the preparation of unsymmetric ethers.[20] The procedure involves S_N2 reactions between an alkyl halide or pseudohalide with an alkoxide anion prepared from an alcohol. However, this method is not useful when the ethers are sensitive to the basic conditions, such as halogenated ethers, due to collateral elimination reaction. In our system, functional groups in alcohols such as halogen, alkene, and alkyne were tolerant as summarized in Table 3. Reactions of **2a** with alcohols bearing halogen, alkene, or alkyne moiety afforded the corresponding propargylic ethers in moderate to good yields, respectively (Table 3, entries 1–4), showing that this method is useful for a direct approach to highly functionalized propargylic ethers. Unfortunately, no etherification occurred when 1,2-propanediol was used as a nucleophile (Table 3, entry 5).

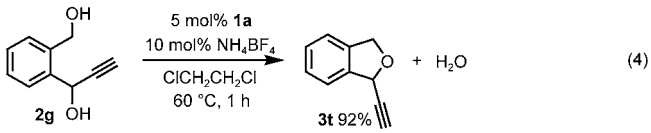
Intramolecular cyclization of propargylic alcohols bearing a hydroxyl group at a suitable position in the same molecule afforded the corresponding cyclic ethers in moderate to high yields with a complete regioselectivity. Thus, cyclization proceeded rapidly with 1-(2-hydroxymethylphenyl)-2-propyn-1-ol (**2g**) to afford the corresponding five-membered-ring product (**3t**) in 92% isolated yield [Eq. (4,)], while 6-hep-

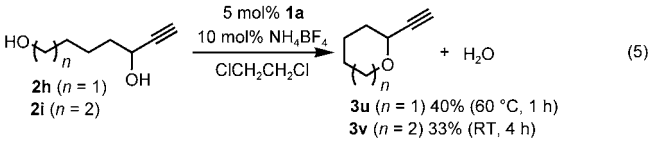
Table 3. Propargylic substitution reactions of propargylic alcohol **2a** with alcohols.[a]

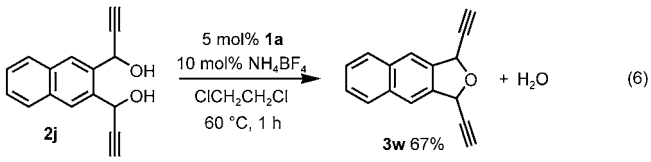


	Alcohol	Propargylic ether (**3**)	Yield [%][b]
1		 **3p**	81
2		 **3q**	77
3		 **3r**	50
4		 **3s**	87
5		–[c]	–

[a] Reactions of propargylic alcohol **2a** (0.60 mmol) with alcohol (3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (15 mL) at 60 °C for 1 h. [b] Isolated yield. [c] A mixture of several unidentified products was formed.



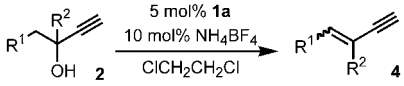


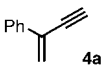
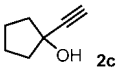
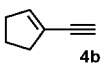
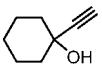
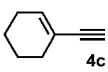
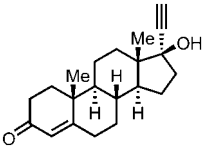
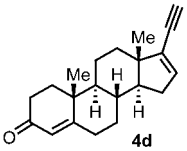
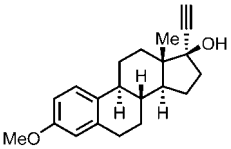
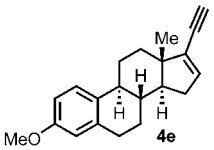


tyne-1,5-diol and 7-octyne-1,6-diol (**2h** and **2i**) gave the corresponding six- and seven-membered-ring products (**3u** and **3v**) in only 40% and 33% yields, respectively [Eq. (5)]. Cyclization proceeded well with a symmetrical diol **2j** to give a mixture of two diastereomeric isomers (**3w**) in 67% yield with the isomer ratio of ca. 2:1 (*dl* isomers : *meso* isomer) [Eq. (6)]

Interestingly, treatment of 2-phenyl-3-butyn-2-ol in EtOH at 60 °C in the presence of a catalytic amount of **1a** and NH_4BF_4 led to the formation of 2-phenyl-1-buten-3-yne (**4a**) in almost quantitative yield (Table 4, entry 1), not the expected ethyl 1-phenyl-2-propynyl ether. Typical results are shown in Table 4. In the absence of **1a**, the formation of the conjugated enyne was not observed at all. This result prompted us to treat suitably 1,1-disubstituted propyn-1-ols in nonpolar solvents, because dehydration can afford the corresponding conjugated enynes, which are important synthetic intermediates. Thus, heating of 1,1-dialkyl-substituted propargylic alcohols (**2c**–**2d**) in $ClCH_2CH_2Cl$ in the presence of **1a** (5 mol%) and NH_4BF_4 (10 mol%) at 60 °C for 15 min gave the corresponding conjugated enynes (**4b** and **4c**) in high yields (Table 4, entries 2 and 3). Similarly, the dehydration of ethisterone and mestranol proceeded smoothly to give the corresponding enynes (**4d** and **4e**) in 86% and 76% isolated yields, respectively (Table 4, entries 4 and 5). Spectroscopic data of these enynes (**4d** and **4e**) were in accordance with those previous-

Table 4. Dehydration of propargylic alcohol (**2**) catalyzed by **1a**.[a]



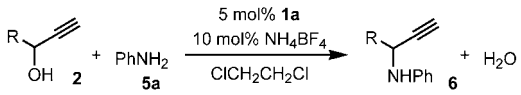
	Propargylic alcohol (**2**)	Conditions T [°C]/t [min]	Enyne (**4**)	Yield [%][b]
1		60/60	 **4a**	95 (91)[c]
2	 **2c**	60/15	 **4b**	86[d]
3	 **2d**	60/15	 **4c**	91[d]
4		60/60	 **4d**	86
5		60/60	 **4e**	76

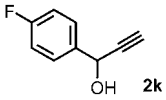
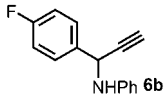
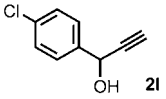
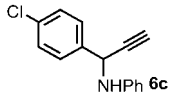
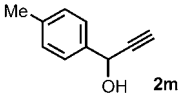
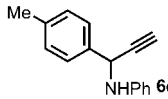
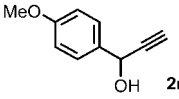
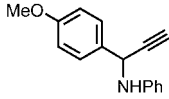
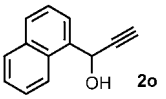
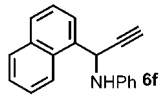
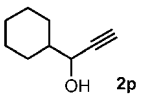
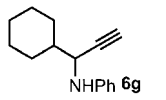
[a] Reactions of propargylic alcohol (**2**; 0.60 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (15 mL). [b] Isolated yield. [c] At RT for 1 h. [d] GLC yield.

ly reported, which were produced by the stoichiometric dehydration of **4d** and **4e** assisted by a monoruthenium complex.[21] Thus, in the absence of nucleophiles, the thiolate-bridged diruthenium complexes promoted the catalytic dehydration of propargylic alcohols into the corresponding conjugated enynes in high yields. Separately, it was confirmed that no dehydration proceeded in the absence of **1a**.

Propargylic substitution reaction with nitrogen-centered nucleophiles: Next, similar substitution with anilines was investigated in the presence of a catalytic amount of **1a**. Typical results are shown in Table 5. For example, treatment of **2a** with five equivalents of aniline (**5a**) in $ClCH_2CH_2Cl$ in the presence of **1a** (5 mol%) and NH_4BF_4 (10 mol%) at 60°C for 1 h afforded *N*-phenyl-1-phenyl-2-propynylamine (**6a**) in 77% isolated (89% GLC) yield (Table 5, entry 1). Similar

Table 5. Propargylic amination of propargylic alcohols (**2**) with aniline (**5a**).[a]



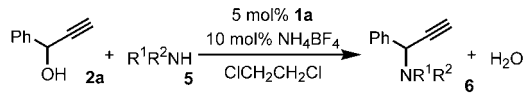
	Propargylic alcohol (**2**)	Propargylic amine (**6**)	Yield [%][b]
1			77 (89)[c]
2			68
3			95
4			82
5			59
6			86
7			71

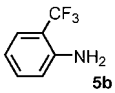
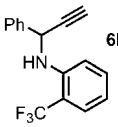
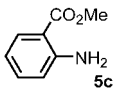
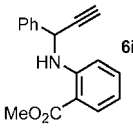
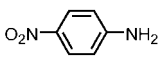
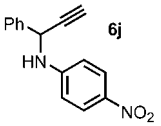
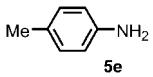
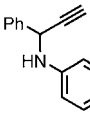
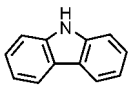
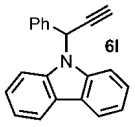
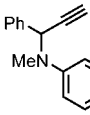
[a] Reactions of propargylic alcohol (**2**; 0.60 mmol) with aniline (**5a**; 3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (18 mL) at 60°C for 1 h. [b] Isolated yield. [c] GLC yield.

to the etherification, the amination proceeded only when the thiolate-bridged diruthenium(Ru^{III}–Ru^{III}) complexes such as **1b** and **1c** were used as catalysts. In these cases, catalytic amination occurred to give **6a** in 64% and 75% yields, respectively. Reactions of various propargylic alcohols with **5a** were carried out in the presence of **1a** and NH_4BF_4. The propargylic substitution reaction of 1-aryl- and 1-alkyl-substituted propargylic alcohols (**2k**–**2p**) with **5a** at 60°C for 1 h proceeded smoothly to afford the corresponding *N*-propargylic anilines (**6b**–**6g**) in moderate to high yields (Table 5, entries 2–7). In contrast, 1,1-diaryl-substituted propargylic alcohols such as **2e** and **2f** did not react at all even after a prolonged reaction time (76 h).

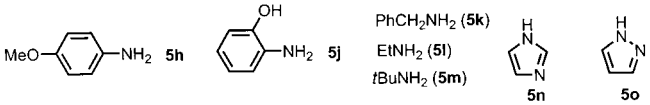
Propargylic amination of **2a** with a variety of anilines was also investigated in the presence of **1a** and NH_4BF_4. Typical results are shown in Table 6. Amination of **2a** with 2-(trifluoromethyl)aniline (**5b**), methyl 2-aminobenzoate (**5c**), and 4-nitroaniline (**5d**) proceeded rapidly to afford the corresponding propargylic amines (**6h**, **6i**, and **6j**) in 68, 82, and 88% isolated yields, respectively (Table 6, entries 1–3). The results indicate that functional groups such as ester and nitro groups are tolerant during the catalytic amination. On the other hand, in the case of 4-methylaniline (**5e**), a longer

Table 6. Propargylic amination of propargylic alcohol **2a** with amines (**5**).[a]

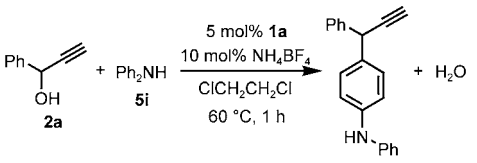


	Amine (**5**)	Conditions T [°C]/t [h]	Propargylic amine (**6**)	Yield [%][b]
1		60/1		68
2		60/1		82
3		60/1		88
4		60/3		64
5		60/1		83
6	PhNHMe **5g**	60/1		16
7		60/5		41

[a] Reactions of propargylic alcohol **2a** (0.60 mmol) with amines (**5**, 3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (18 mL). [b] Isolated yield.



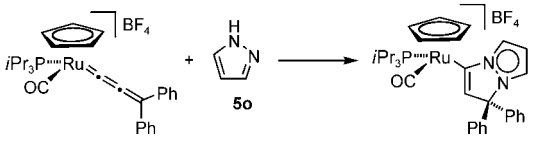
reaction time (3 h) was required to produce *N*-propargylic 4-methylaniline (**6k**) in 64% yield (Table 6, entry 4), while no reaction occurred with 4-methoxyaniline (**5h**) even for 3 h. Thus, the introduction of an electron-releasing moiety such as *p*-methyl or *p*-methoxy group in the aromatic group of anilines decreased the reaction rate. Propargylation of aromatic ring proceeded instead of propargylic amination when **2a** was treated with *N*,*N*-diphenylamine (**5i**) under the same reaction conditions [Eq. (7)].



(7)

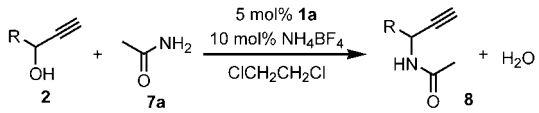
It is considered that two phenyl groups around the nitrogen atom of *N*,*N*-diphenylamine and low basicity of **5i** may inhibit the amination. The propargylation of a benzene ring of **5i** proceeded smoothly. Previously, we reported the propargylic substitution reaction of **2a** with phenol to produce phenyl 1-phenyl-2-propynyl ether in high yield [Eq. (1)].[15] For comparison of the reactivity between hydroxy and amino groups in the aromatic ring, the reaction of **2a** with 2-aminophenol (**5j**) was carried out, but **2a** was almost completely recovered together with the formation of a small amount of unidentified products. No further information was obtained as to the unreactivity of **5j**. Unfortunately, the use of *primary* alkylamines such as benzylamine (**5k**), ethylamine (**5l**), and *tert*-butylamine (**5m**) for this propargylic amination was in vain, showing that amines with high basicity are not applicable to the propargylic amination (vide infra) under these catalytic conditions.

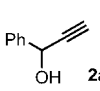
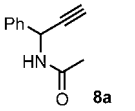
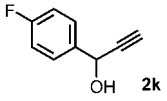
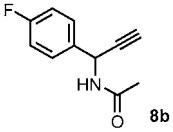
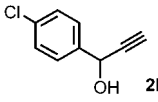
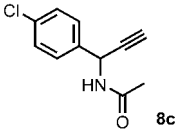
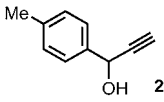
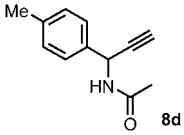
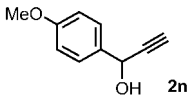
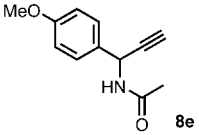
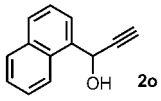
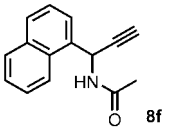
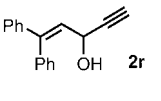
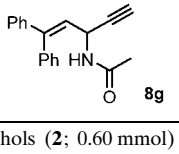
Interestingly, carbazole (**5f**) worked effectively as an aminating reagent to produce *N*-propargylic 9-*H*-carbazole (**6l**) in 83% yield under the same reaction conditions (Table 6, entry 5). In contrast, the reaction with *secondary* alkylamines, such as *N*-methylaniline (**5g**), was sluggish under identical conditions and a prolonged time was required to improve the yield of the propargylic amine (**6m**) (Table 6, entries 6 and 7). Previously, Esteruelas and co-workers reported the stoichiometric reaction of a cationic allenylidene complex $[Ru(Cp)(C{=}C{=}CPh_2)(CO)(P\mathit{i}Pr_3)]BF_4$ with pyrazole to afford $[Ru(Cp)\{C{=}CHC(Ph)_2N(CH)_3N\}(CO)(P\mathit{i}Pr_3)]BF_4$ as a result of the addition of pyrazole to the allenylidene moiety.[22] However, the reaction using both imidazole (**5n**) and pyrazole (**5o**) did not give any of the expected products under our catalytic conditions.



The scope of the propargylic amination extends beyond simple amine substrates. For example, selected amides, lactams, and sulfonamides gave useful amidated products directly from propargylic alcohols. Reactions of propargylic alcohols with an acyclic amide such as acetamide (**7a**) were investigated at first. Treatment of **2a** with five equivalents of **7a** at 60°C for 1 h in the presence of **1a** (5 mol%) and NH_4BF_4 (10 mol%) gave the corresponding propargylic amide (**8a**) in 73% isolated yield with a complete regioselectivity (Table 7, entry 1). The amidation proceeded smoothly even at room temperature for 2 h, with **8a** being obtained in 79% isolated yield. Typical results are shown in Table 7. A variety of propargylic alcohols were available for this catalytic amidation. Introduction of a *p*-fluoro, *p*-chloro, *p*-methyl, or *p*-methoxy substituent to the aromatic ring of

Table 7. Propargylic amidation of propargylic alcohols (**2**) with acetamide **7a**.[a]



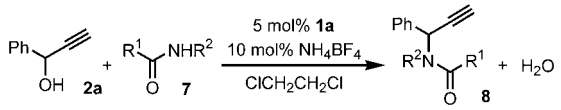
	Propargylic alcohol (**2**)	Propargylic amine (**8**)	Yield [%][b]
1	 **2a**	 **8a**	73 (79)[c]
2	 **2k**	 **8b**	62
3	 **2l**	 **8c**	50
4	 **2m**	 **8d**	58
5	 **2n**	 **8e**	70
6	 **2o**	 **8f**	42
7	 **2r**	 **8g**	41[d]

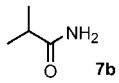
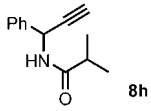
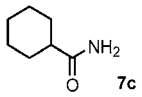
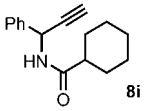
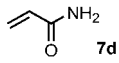
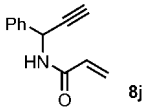
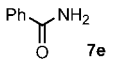
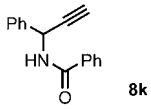
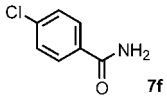
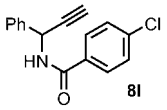
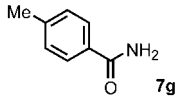
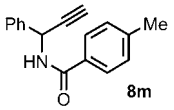
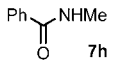
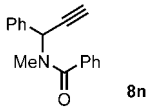
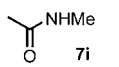
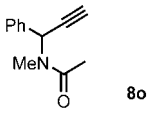
[a] Reactions of propargylic alcohols (**2**; 0.60 mmol) with acetamide **7a** (3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (18 mL) at 60°C for 1 h. [b] Isolated yield. [c] At RT for 2 h. [d] 10 mol% of **1a** was used.

2a and the use of naphthyl moiety slightly decreased the yield of the amidation product (Table 7, entries 2–6). 1-Alkenyl-substituted propargylic alcohol (**2r**) was converted into the corresponding alkenyl propargylic amide (**8g**), but in low yield (Table 7, entry 7). Unfortunately, no amidation occurred when 1-cyclohexyl-2-propyn-1-ol (**2p**) was used in the reaction with **7a**.

Reactions of **2a** with other acyclic amides were investigated in the presence of **1a**. Typical results are shown in Table 8. Propargylation of saturated (**7b** and **7c**) and unsaturated (**7d**) amides and benzamides (**7e**–**7h**) proceeded smoothly to give the corresponding propargylic amides in high yields (Table 8, entries 1–7). In sharp contrast to the high reactivity of acetamide (**7a**), the reaction of **2a** with *N*-methyl acetamide (**7i**) was sluggish; 64% yield of **8o** being obtained by using 10 mol% of **1a** as catalyst (Table 8, entry 8). In addition, propargylation of sulfonamides such as methanesulfonamide (**7j**) and *p*-toluenesulfonamide (**7k**) occurred easily to give the corresponding propargylic amides (**8p** and **8q**) (Table 9, entries 1 and 2), which may be transformed into the corresponding propargylic amines by reductive method.[23] Typical results are shown in Table 9. Reactions of **2a** with four- and five-membered-ring lactams (**7l** and **7m**) proceeded in the presence of **1a** and the corresponding propargylic lactams (**8r** and **8s**) were obtained in 78% and 74% yields, respectively (Table 9, entries 3 and 4). However, the six-membered-ring lactam **7n** reacted with **2a** to afford the corresponding propargylic lactam **8t** in only poor yield (Table 9, entry 5). The molecular structures of **8j** and **8q** were unambiguously clarified by X-ray analysis.

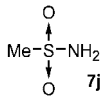
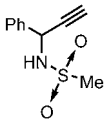
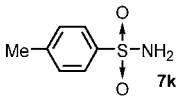
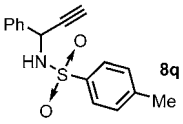
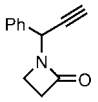
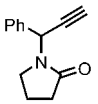
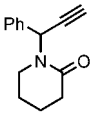
Table 8. Propargylic amidation of propargylic alcohol **2a** with amides (**7**).[a]



	Amide (**7**)	Propargylic amide (**8**)	Yield [%][b]
1	 **7b**	 **8h**	72
2	 **7c**	 **8i**	56
3	 **7d**	 **8j**	71
4	 **7e**	 **8k**	71
5	 **7f**	 **8l**	61
6	 **7g**	 **8m**	67
7	 **7h**	 **8n**	64
8	 **7i**	 **8o**	64[c]

[a] Reactions of propargylic alcohol (**2a**) (0.60 mmol) with amide (**7**; 3.0 mmol) were carried out in the presence of **1a** and NH_4BF_4 in $ClCH_2CH_2Cl$ (18 mL) at 60°C for 1 h. [b] Isolated yield. [c] 10 mol% of **1a** was used.

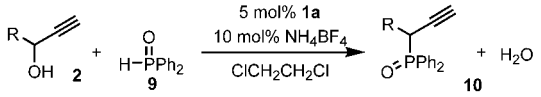
Table 9. Propargylic amidation of propargylic alcohol **2a** with amides (**7**).[a]

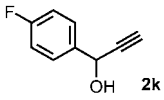
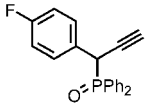
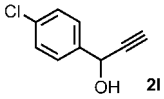
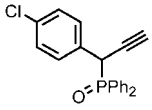
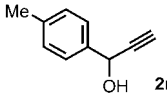
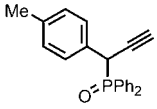
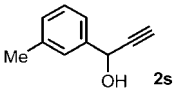
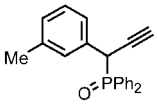
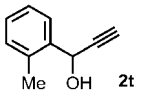
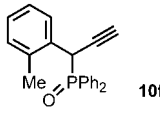
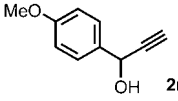
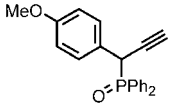
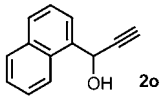
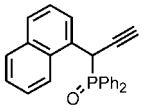
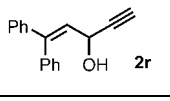
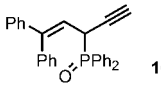
	Amide (**7**)	Conditions T [°C]/t [h]	Propargylic amide (**8**)	Yield [%][b]
1	 **7j**	60/1	 **8p**	63
2	 **7k**	60/1	 **8q**	52
3	 **7l**	60/1	 **8r**	78
4	 **7m**	60/1	 **8s**	74
5	 **7n**	60/3	 **8t**	18

[a] Reactions of propargylic alcohol **2a** (0.60 mmol) with amide (**7**; 3.0 mmol) were carried out in the presence of **1a** (5 mol%) and NH_4BF_4 (10 mol%) in $ClCH_2CH_2Cl$ (18 mL). [b] Isolated yield.

Propargylic substitution reaction with phosphorus-centered nucleophiles: Diphenylphosphine oxide (**9**) could be used as a phosphorus-centered nucleophile. Treatment of **2a** with five equivalents of diphenylphosphine oxide in $ClCH_2CH_2Cl$ in the presence of **1a** (5 mol%) and NH_4BF_4 (10 mol%) at 25°C for 1 h gave the corresponding propargylic diphenylphosphine oxide (**10a**) in 84% yield with a complete regioselectivity. Typical results are shown in Table 10. When the same reaction was carried out at 60°C, **10a** was produced in only 56% yield together with some undesirable unidentified

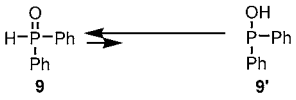
Table 10. Reactions of propargylic alcohols (**2**) with diphenylphosphine oxide (**9**).[a]



	Propargylic alcohol (**2**)	Conditions T [°C]/t [h]	Propargylic phosphine (**10**)	Yield [%][b]
1	 **2a**	25/1	 **10a**	84 (56)[c]
2	 **2k**	25/1	 **10b**	81
3	 **2l**	25/1	 **10c**	74
4	 **2m**	25/1	 **10d**	84
5	 **2s**	25/18	 **10e**	78
6	 **2t**	25/1	 **10f**	87
7	 **2n**	25/1	 **10g**	88
8	 **2o**	25/2	 **10h**	90
9	 **2r**	25/2	 **10i**	67

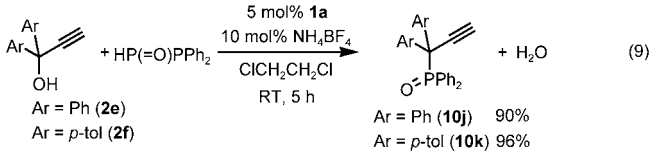
[a] Reactions of propargylic alcohol (**2**; 0.60 mmol) with diphenylphosphine oxide (**9**; 3.0 mmol) were carried out in the presence of **1a** and $ClCH_2CH_2Cl$ (18 mL). [b] Isolated yield. [c] At 60 °C for 1 h.

products (Table 10, entry 1). Detailed investigation of the reaction at 60 °C revealed that double phosphinylation of **2a** proceeded to afford the corresponding 2,3-bis(diphenylphosphinyl)-3-phenyl-1-propene as a minor product. Similar to the amination and amidation, the propargylation of phosphine oxide proceeded only when the thiolate-bridged dirutheniumcomplex (Ru^{III}–Ru^{III}) (**1a**) was used as catalyst. It is known that an equilibrium is present between **9** and its tautomer (**9′**, diphenylphosphinous acid) by migration of a hydrogen atom from a phosphorus atom to an oxygen atom [Eq. (8)].[24] In this catalytic reaction, the phosphorus atom of diphenylphosphinous acid may attack the C_γ atom of the allenylidene intermediates (vide infra).



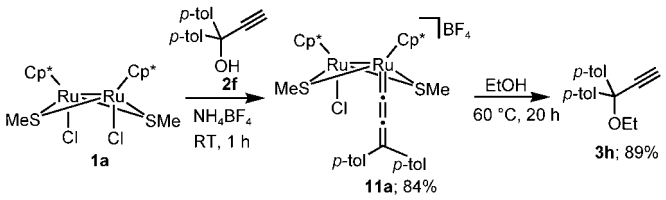
(8)

Various propargylic alcohols could be employed for the propargylation of phosphine oxide. In most cases, higher yields of products were obtained when the catalytic reactions were carried out at 25 °C (Table 10, entries 2–9). No propargylation occurred in the reaction of 1-cyclohexyl-2-propyn-1-ol (**2p**) with diphenylphosphine oxide even at 60 °C, while the reaction of 1,1-diaryl propargylic alcohols (**2e** and **2f**) proceeded to give the corresponding propargylic phosphine oxide (**10j** and **10k**) in 90 % and 96 % isolated yields [Eq. (9)]. On the other hand, diphenylphosphine (PPh_2H) could not be used as a phosphorus-centered nucleophile for this catalytic reaction and thus, the reaction of **2a** with diphenylphosphine in the presence of **1** resulted in the formation of an unstable and unidentified product (by ^{31}P NMR spectroscopy). The high basicity of diphenylphosphine, which might coordinate to ruthenium, may be one of the reasons for this unsuccessful substitution. The molecular structures of **10a** and **10b** were unambiguously clarified by X-ray analysis.



(9)

Isolation of intermediate allenylidene complexes and their reactivity: As described in our preliminary communication, an allenylidene complex (**11a**) could be isolated as an intermediate by the reaction of **1a** with one equivalent of propargylic alcohol **2f** in the presence of NH_4BF_4 in EtOH at room temperature for 1 h (Scheme 2).[15] The molecular structure of **11a** was determined previously by X-ray crystallography,[15] an ORTEP drawing of which is shown in



Scheme 2. Isolation of an allenylidene complex and its reactivity.

Figure 1 with selected bond lengths and angles in Table 11.[15] The ORTEP view displays an unsymmetrically substituted dinuclear structure, in which the η^1-allenylidene and Cl ligands are coordinated to the respective ruthenium

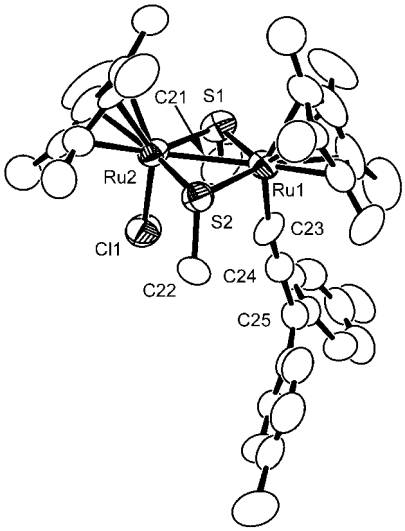
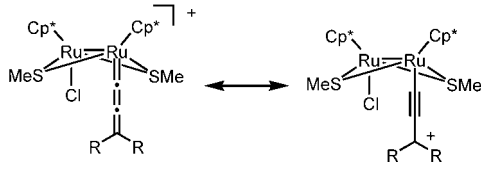


Figure 1. ORTEP drawing for the cationic part of **11a**. Hydrogen atoms are omitted for clarity.

Table 11. Selected bond lengths [Å] and angles [°] for **11a**.[15]

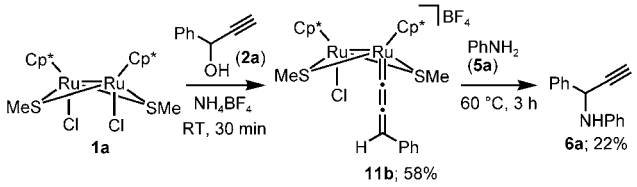
Ru1–Ru2	2.768(3)	Ru2–S2	2.312(6)
Ru1–S1	2.316(7)	C23–C24	1.20(3)
Ru1–S2	2.303(6)	C24–C25	1.47(3)
Ru1–C23	1.91(2)	S1–C21	1.80(3)
Ru2–Cl1	2.396(7)	S2–C22	1.86(2)
Ru2–S1	2.307(7)		
Ru2-Ru1-C23	97.9(7)	Ru1-S1-Ru2	73.6(2)
S1-Ru1-S2	106.3(3)	Ru1-S2-Ru2	73.7(2)
Ru1-Ru2-Cl1	94.3(2)	Ru1-C23-C24	171.0(2)
S1-Ru2-S2	106.2(2)	C23-C24-C25	174.0(2)

centers in a mutual *cis* configuration, and it is in a full accordance with the NMR and IR spectroscopic observations. The allenylidene moiety C23-C24-C25 is almost linear (174(2)°). The C23–C24 bond (1.20(3) Å) is significantly shorter than the normal carbon–carbon double bond, whereas the C24–C25 bond (1.47(3) Å) is significantly longer. These data suggest the important contribution of the resonance structure as shown in Scheme 3. The intramolecular distance between the two ruthenium atoms (2.768(3) Å) corresponds to a Ru–Ru single bond (2.71–3.02 Å).[25] The complex **11a** offers a rare example of a multinuclear allenyl-



Scheme 3. The important contribution of the resonance structure of the allenylidene complexes.

idene compound with only a terminal allenylidene ligand on the bimetallic center.[7] As described earlier, the stoichiometric reaction of **11a** in EtOH at 60 °C for 20 h afforded **3h** in 89 % GLC yield.[15] Here, stoichiometric reactions between the allenylidene complex $[(Cp^*)RuCl(\mu_2\text{-}SMe)_2Ru(Cp^*)(C{=}C{=}CHPh)]BF_4$ (**11b**)[17a] and anilines were investigated. Treatment of **11b** with ten equivalents of aniline (**5a**) in $ClCH_2CH_2Cl$ at 60 °C for 3 h gave propargylic amine **6a** in 22 % isolated yield based on **11b** (Scheme 4). In addi-



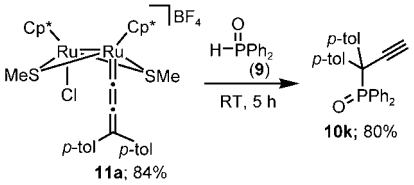
Scheme 4. Stoichiometric reaction of the allenylidene complex **11b** with aniline.

tion, the propargylic amination of **2a** with **5a** in the presence of 5 mol % of **11b** proceeded to afford **6a** in 71 % yield. These results indicate that the propargylic substitution reaction generally proceeds via allenylidene complexes like **11b**.

Theoretical studies clearly indicate that the C_α and C_γ atoms of the allenylidene moiety are electrophilic centers, while the C_β atom works as a nucleophilic site.[7] It is known that both primary and secondary amines attack on the C_α atom in allenylidene complexes such as $[CpRu(C{=}C{=}CPh_2)(CO)(P\mathit{i}Pr_3)]BF_4$ to afford the corresponding azoniabutadienyl complexes $[CpRu\{C(CH{=}CPh_2){=}NR''_2\}(CO)(P\mathit{i}Pr_3)]BF_4$ (R'' = aryl, alkyl, alkenyl, or H).[26] In contrast, the nucleophilic attack of amine on the allenylidene C_γ atom is limited to the reaction of cationic allenylidene complex $[CpRu(C{=}C{=}CPh_2)(PPh_3)_2]PF_6$ with dimethylamine to form $[CpRu\{C{\equiv}CCPh_2(NHMe_2)\}(PPh_3)_2]PF_6$.[27] In our system, the steric bulkiness of the two Cp* ligands present at diruthenium core seems to inhibit the nucleophilic attack of the amine on the C_α atom in the allenylidene ligand.

Thus, the amine attacks regioselectively on the C_γ atom in allenylidene complexes like **11b**.

The stoichiometric reaction of an allenylidene complex (**11a**) with diphenylphosphine oxide (**9**) gave propargylic phosphine oxide **10k** in 80% yield (Scheme 5), indicating



Scheme 5. Stoichiometric reaction of the allenylidene complex **11a** with diphenylphosphine oxide.

that the phosphorus–carbon bond formation also proceeds through the nucleophilic attack of the phosphorus atom to the C_γ atom of the allenylidene ligand. Several examples of nucleophilic addition of secondary and tertiary phosphines to the C_γ atom of the ruthenium and rhenium allenylidene complexes have already been reported to afford the corresponding γ-phosphonioalkynyl and their rearranged α-phosphonioallenyl complexes.[28]

Catalytic reaction pathway for propargylic substitution—amination as a representative example: The relative reactivity of substituted anilines ($XC_6H_4NH_2$, X = *p*-Me, H, *p*-Cl) for the reactions with **2a** in the presence of **1a** was determined (Scheme 6 and Table 12). The relative rates were determined by the conversion of **2a** when conversions were low (<10%). The rate data correlate well with the Hammett linear free-energy relationship with use of σ values (Figure 2). Better correlation ($\rho = 2.3$) was obtained with a σ value rather than σ^+, suggesting the absence of electrophilic species in the rate-determining step. This result indicates that the attack of anilines on the C_γ atom in the allenylidene ligand is not involved in the rate-determining step. The acidity of conjugated anilines on an alkynyl complex (**C′**), which is formed after the attack of anilines on the C_γ atom of the allenylidene complex (**B**), is considered to be the most important factor to determine the rate of the catalytic reactions of **2a** with anilines (Scheme 7). Thus, the higher acidity of the proton of conjugated anilines in the alkynyl complex promotes the hydrogen atom shift onto the C_β atom on the ligand to give the vinylidene complex (**D′**). This proton 1,3-migration step should be involved in the rate-determining step. In fact, the proton migration did not occur in the reactions with alkylamines of low acidity, such as benzylamine and ethylamine, and also with anilines bearing electron-releasing moiety at aromatic ring, such as *p*-methoxyaniline. On the other hand, good correlation ($\rho = -0.39$) was also obtained with a σ value when the relative reactivity of substituted propargylic alcohol ($XC_6H_4CH(OH)C{\equiv}CH$, X = *p*-Me, H, *p*-Cl) with **5a** was determined in the presence of **1a**

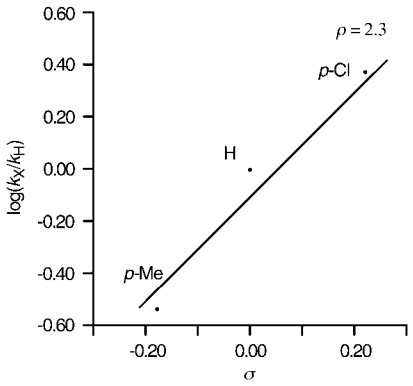
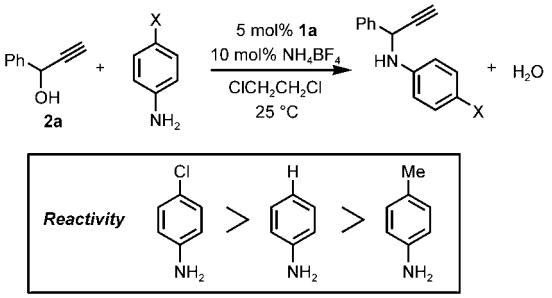


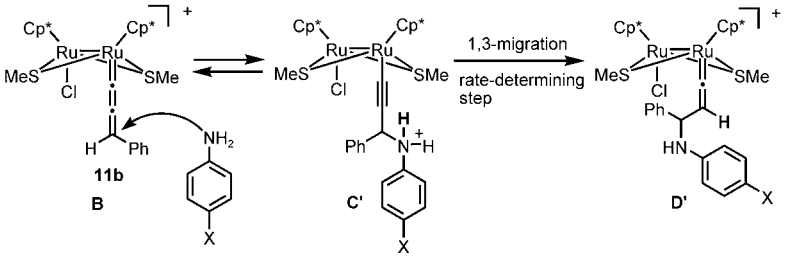
Figure 2. Plot of $\log(k_X/k_H)$ vs σ values for the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohol (**2a**) with substituted anilines.



Scheme 6. The relative reactivity of substituted anilines.

Table 12. Relative rate constants for the ruthenium-catalyzed propargylic substitution reactions of propargylic alcohol (**2a**) with substituted anilines.

X in $XC_6H_4NH_2$	σ	(σ^+)	k_X/k_H	$\log(k_X/k_H)$
p-Me	−0.17	(−0.31)	0.278	-0.556
H	0	(0)	0	0
p-Cl	0.23	(0.11)	2.444	0.388

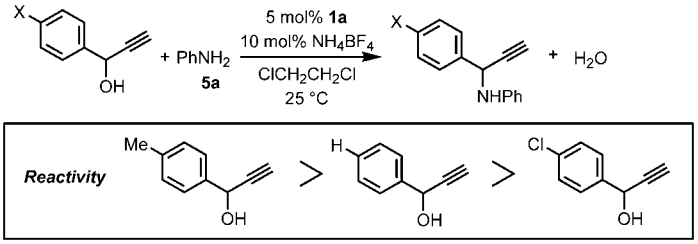


Scheme 7. The acidity of conjugated anilines on an alkynyl complex is considered to be the most important factor.

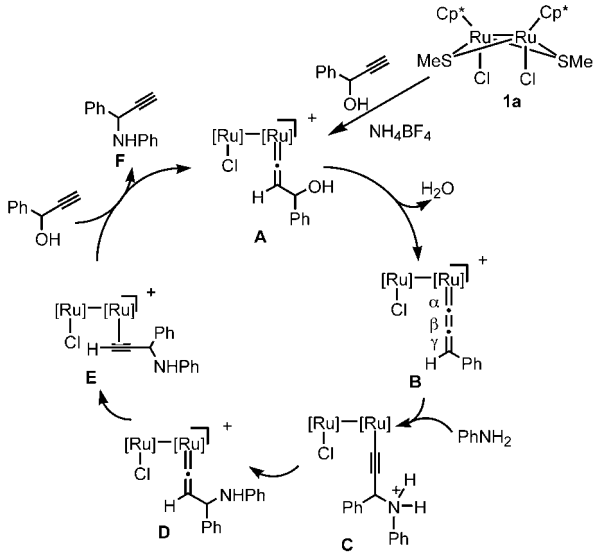
(Scheme 8). The ρ value, however, was quite smaller than that obtained for the reaction of **2a** with anilines.

By considering all the experimental evidence, a reaction pathway of this catalytic propargylic substitution reaction is proposed in Scheme 9 for amination with aniline as a representative example. Initially, a vinylidene complex (**A**) is formed in the reaction of **1a** with propargylic alcohol in the presence of NH_4BF_4. Dehydration of **A** leads to an allenylidene complex (**B**), and subsequent nucleophilic attack of aniline on the C_γ atom in the allenylidene ligand results in the formation of an alkynyl complex (**C**), in which the higher acidity of the proton of conjugated anilines in **C** promotes a hydrogen atom shift into the C_β atom on the ligand to give another vinylidene complex (**D**). Thus, the addition of NH bond of the amine to the C_γ=C_β double bond of the allenylidene group takes place to yield the vinylidene complex **D**. The complex **D** is then transformed into the η^2-coordinated propargylic amine tautomer (**E**), which liberates the product propargylic amine (**F**) by the reaction with a propargylic alcohol and regenerates the complex **A**.[8,29]

Although reactions in the presence of many types of ruthenium complexes have been carried out until now, only the thiolate-bridged diruthenium complexes can promote the catalytic propargylic substitution reaction. The key point to promote our catalytic reaction by using the thiolate-bridged diruthenium complexes is considered to be the ease of the ligand exchange steps in the catalytic cycle (**D**→**E** in Scheme 9). In fact, Gimeno and co-workers reported the reaction of the allenylidene complexes with nucleophiles to give the corresponding vinylidene complexes, and confirmed that the ligand exchange of the vinylidene moiety with another ligand did not proceed smoothly to give the corresponding terminal alkyne, which is derived from the vinylidene ligand.[8] In order to obtain some information of the ease of ligand exchange for our catalytic reaction by using the thiolate-bridged diruthenium complexes, the following stoichiometric reactions between the allenylidene complex $[(Cp^*)RuCl(\mu_2\text{-}SMe)_2Ru(Cp^*)(C{=}C{=}CHPh)]BF_4$ (**11b**)[17a] and anilines were investigated in the presence of a variety of an additive (Table 13). Although no improved yield was observed in the presence of NH_4BF_4 (Table 13, entry 2), the addition of either NH_4Cl or another terminal alkyne much improved the yield of **6a** (Table 13, entries 3 and 4). The reaction of **11b** with **5a** in the presence of propargylic alcohol **2k** gave **6a** in 53% yield together with **6b** in 49% yield (Table 13, entry 5). These results indicate that the liberation of product **6a** (or **F**′) from the intermediate **E**′ may be accelerated by a ligand exchange[8,29] with NH_4Cl, producing a stable starting complex **1a** (Scheme 10). In the case of the addition of another terminal alkyne, a similar ligand exchange[8,26] from **E**′ with the alkyne occurs smoothly to give the product **F**′ and the corresponding vinylidene complex **A**′ (Scheme 11). Thus, it has now been found that the ligand exchange of the vinylidene moiety in the thiolate-bridged diruthenium complexes proceeds quite smoothly, clarifying the key point for our catalytic reaction.

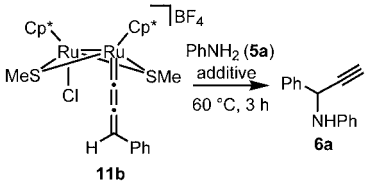


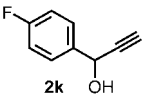
Scheme 8. The relative reactivity of substituted propargylic alcohols.



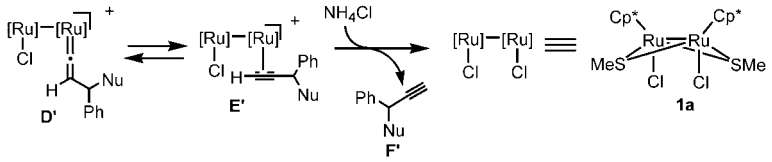
Scheme 9. A reaction pathway of the catalytic propargylic substitution reaction.

Table 13. Reactions of allenylidene complex **11b** with aniline (**5a**) in the presence of additive.[a]

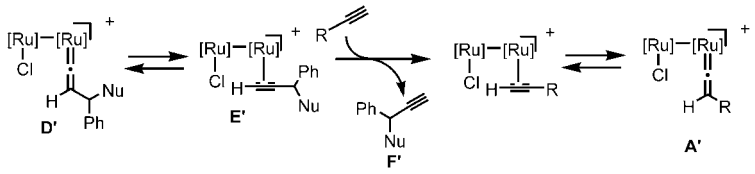


	Additive	Equiv[b]	Yield of **6a** [%][c]
1	–		22[d]
2	NH_4BF_4	5	21
3	NH_4Cl	5	56
4	CO_2Me	1	39
5		1	53[e]

[a] Reactions of allenylidene complex **11b** (0.02 mmol) with aniline (**5a**; 0.2 mmol) were carried out in the presence of an additive in $ClCH_2CH_2Cl$ (2 mL). [b] Equivalents of additive relative to **11b**. [c] GLC yield. [d] Isolated yield. [e] **6b** was also obtained in 49% GLC yield.



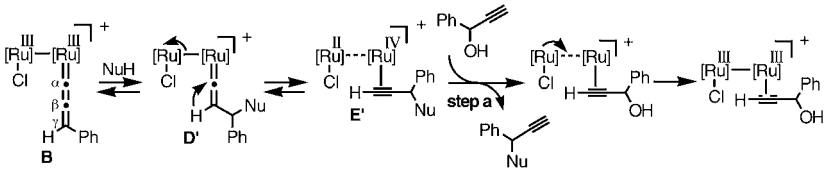
Scheme 10. The liberation of product from the intermediate may be accelerated by a ligand exchange with NH_4Cl.



Scheme 11. The liberation of product from the intermediate may be accelerated by a ligand exchange with another terminal alkyne.

The above results of the stoichiometric and catalytic reactions indicate that allenylidene complexes such as **11a** are one of the key intermediates for the propargylic substitution reactions. However, we have previously reported one example of the propargylic substitution reaction of propargylic alcohols bearing not only terminal acetylene but also internal acetylene units.[16] At present, we should also consider the possibility of Nicholas type activation by coordination of acetylene unit of propargylic alcohols on the diruthenium sites.[2]

As described in our previous paper,[30] we believe that the reason why only the diruthenium complexes promote the ligand exchange step more easily in our catalytic reaction should be that one Ru moiety, which is not involved in the allenylidene formation, works as an electron pool or a mobile ligand to another Ru site (Scheme 9), by taking into account of the theoretical report of synergistic effects of two equal Rh metals in the dirhodium-catalyzed reaction between diazo compound and alkane.[31] To prove the possibility of the synergistic effects of two ruthenium atoms as described in Scheme 12, a series of chalcogenolate (S, Se, Te)-

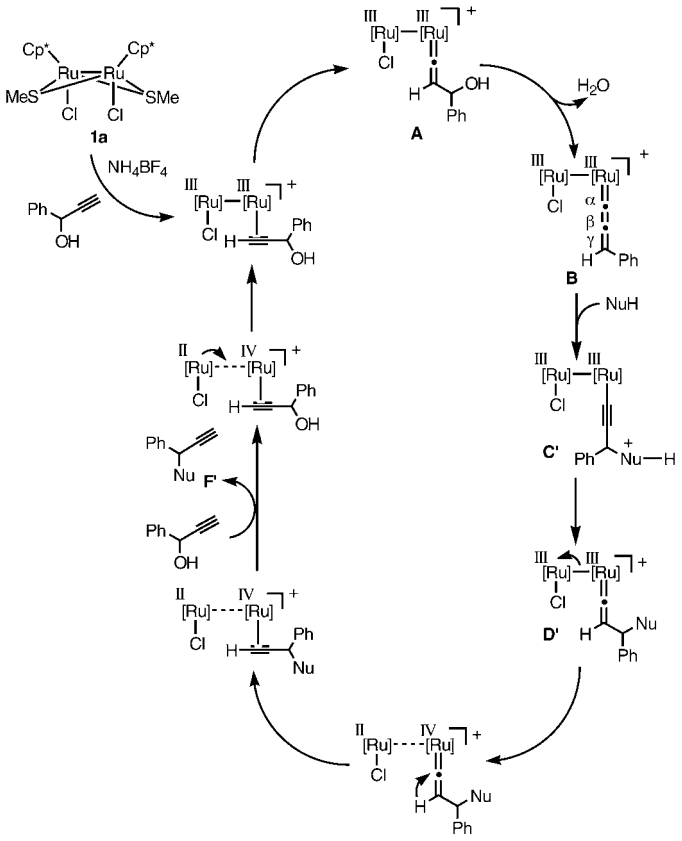


Scheme 12. The possibility of the synergistic effects of two ruthenium atom s.

bridged diruthenium complexes (neutral and cationic) have been prepared and their catalytic activities toward the propargylic substitution reactions as well as electronic properties have been investigated to prove the proposed reaction pathway.[30] Results of both catalytic and stoichiometric reactions and electronic behaviors of the complexes indicate that the ease of the charge transfer from one Ru atom to the other in the complexes (synergistic effect) may be one of the important factors to promote the ligand exchange (step a), which is a key step for the catalytic reaction.[30] As a result, we consider that newly obtained experimental results support our previous proposal for the catalytic reaction pathway. Thus, our new findings described in this paper provide the basis of the catalytic reaction pathway, which we have already proposed in our previous paper. Finally, we summarized a full reaction pathway of this catalytic propargylic substitution reaction in Scheme 13 by using NuH as a nucleophile. Further work is currently in progress aiming at the elucidation of the more detailed reaction mechanism assisted by quantum calculations.

Conclusion

A general procedure for the catalytic propargylic substitution reactions of propargylic alcohols with heteroatom-centered nucleophiles is reported. Oxygen-, nitrogen-, and phosphorus-centered nucleophiles such as alcohols, amines, amides, and phosphine oxide are available for this catalytic reaction. The most characteristic feature of this reaction is the direct use of propargylic alcohols as effective substrates, the only expected byproduct in stoichiometry being water (H_2O). It is noteworthy that only the thiolate-bridged diruthenium complexes promote this catalytic reaction. Results of some stoichiometric and catalytic reactions indicate that the catalytic propargylic substitution reaction proceeds via allenylidene complexes, for which the attack of nucleophiles to the C_γ atom of the allenylidene ligand is a key step. Furthermore, the key point to promote the catalytic reaction by using the thiolate-bridged diruthenium complexes is considered to be the ease of the ligand exchange step between a vinylidene ligand on the diruthenium complexes and another propargylic alcohol in the catalytic cycle. Our new findings described in this paper provide the basis of the catalytic reaction pathway, which we have already proposed in our previous paper. The procedure in this paper provides a versatile and direct method for propargylic substitution of propargylic alcohols.



Scheme 13. A full reaction pathway of the catalytic propargylic substitution reaction.

Experimental Section

General methods: ^{1}H NMR (400, 300, and 270 MHz) and ^{13}C NMR (100, 75, and 67.8 MHz) spectra were recorded using $CDCl_3$ as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

Materials: Thiolate-bridged diruthenium complexes[15,30] (**1**) and the allenylidene complexes[15,17] (**11**) were prepared according to our previous procedures. Propargylic alcohol (**2a**) was a commercial product. Other propargylic alcohols were prepared by the reactions of the corresponding aldehydes with ethynylmagnesium bromide. Propargylic products (**3o**,[19] **3u**,[32] **4d**,[21] and **4e**[21]) were previously prepared by us or other groups.

Ruthenium-catalyzed propargylic substitution reactions of propargylic alcohols with nucleophiles: A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with EtOH catalyzed by **1a** is described below. Complex **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) were placed in a 20 mL flask under N_2. Anhydrous EtOH (15 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (0.60 mmol), the reaction flask was kept at 60 °C for 15 min. The reaction mixture was treated with brine (50 mL) and then extracted with diethyl ether (20 mL × 3). The ether layer was dried over anhydrous $MgSO_4$. For isolation, the extract was concentrated under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO_2) with EtOAc-*n*-hexane (1/9) to give **3a** as a pale yellow oil (0.53 mmol, 88 % yield).

Data for 3a: ^{1}H NMR: δ = 1.26 (t, J = 7.0 Hz, 3H), 2.63 (d, J = 2.0 Hz, 1H), 3.55 (qd, J = 7.0, 8.8 Hz, 1H), 3.75 (qd, J = 7.0, 8.8 Hz, 1H), 5.16 (d, J = 2.0 Hz, 1H), 7.33–7.40 (m, 3H), 7.52 ppm (d, J = 7.3 Hz, 2H); ^{13}C NMR: δ = 15.1, 63.9, 71.1, 75.3, 81.8, 127.3, 128.4, 128.5, 138.3 ppm; IR (neat): $\tilde{\nu}$ = 2114 (C≡C), 3293 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{11}H_{12}O$: C 82.46, H 7.55; found: C 82.56, H, 7.47.

Data for 3b: Yield 84 %; a pale yellow oil; ^{1}H NMR: δ = 2.66 (d, J = 2.5 Hz, 1H), 3.45 (s, 3H), 5.09 (s, 1H), 7.34–7.40 (m, 3H), 7.51 ppm (d, J = 7.8 Hz, 2H); ^{13}C NMR: δ = 55.9, 72.7, 75.8, 81.2, 127.3, 128.5, 128.5, 137.9 ppm; IR (neat): $\tilde{\nu}$ = 2114 (C≡C), 3293 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{10}H_{10}O$: C 82.16, H 6.89; found: C 82.33, H 6.77.

Data for 3c: Yield 91 %; a pale yellow oil; ^{1}H NMR: δ = 1.22 (d, J = 5.6 Hz, 3H), 1.25 (d, J = 5.6 Hz, 3H), 2.58 (d, J = 2.0 Hz, 1H), 3.98 (sept, J = 5.6 Hz, 1H), 5.20 (s, 1H), 7.32–7.39 (m, 3H), 7.51 ppm (d, J = 8.0 Hz, 2H); ^{13}C NMR: δ = 21.6, 22.7, 68.5, 69.7, 74.6, 82.6, 127.2, 128.3, 128.5, 139.0 ppm; IR (neat): $\tilde{\nu}$ = 2114 (C≡C), 3293 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{12}H_{14}O$: C 82.72, H 8.10; found: C 82.61, H 8.07.

Data for 3d: Yield 75 %; a pale yellow oil; ^{1}H NMR: δ = 0.89 (t, J = 6.8 Hz, 3H), 1.13 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 6.0 Hz, 3H), 1.30 (m, 4H), 1.45 (m, 2H), 1.69 (m, 2H), 2.37 (s, 1H), 3.90 (sept, J = 6.0 Hz, 1H), 4.08 ppm (t, J = 6.4 Hz, 1H); ^{13}C NMR: δ = 14.0, 21.2, 22.6, 23.2, 25.0, 31.5, 36.1, 66.6, 69.7, 72.5, 84.1 ppm; IR (neat): $\tilde{\nu}$ = 2110 (C≡C), 3312 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{11}H_{20}O$: C 78.51, H 11.98; found: C 78.11, H 11.58.

Data for 3e: Yield 54 %; a pale yellow oil; ^{1}H NMR: δ = 1.20 (t, J = 6.8 Hz, 3H), 1.73 (m, 4H), 1.92–1.98 (m, 4H), 2.45 (s, 1H), 3.58 ppm (q, J = 6.8 Hz, 2H); ^{13}C NMR: δ = 15.7, 23.2, 39.4, 60.0, 72.2, 79.7, 85.8 ppm; IR (neat): $\tilde{\nu}$ = 2108 (C≡C), 3306 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_9H_{14}O$: C 78.21, H 10.21; found: C 78.45, H 10.33.

Data for 3f: Yield 57 %; a pale yellow oil; ^{1}H NMR: δ = 1.21 (t, J = 6.8 Hz, 3H), 1.26 (m, 4H), 1.52–1.66 (m, 4H), 1.89 (m, 2H), 2.44 (s, 1H), 3.62 ppm (q, J = 6.8 H, 2Hz); ^{13}C NMR: δ = 15.8, 22.7, 25.4, 29.7, 37.1, 58.4, 73.2, 85.6 ppm; IR (neat): $\tilde{\nu}$ = 2103 (C≡C), 3308 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{10}H_{16}O$: C 78.90, H 10.59; found: C 78.51, H 10.48.

Data for 3g: Yield 62 %; a pale yellow oil; ^{1}H NMR: δ = 1.27 (t, J = 7.2 Hz, 3H), 2.86 (d, J = 2.0 Hz, 1H), 3.54 (q, J = 7.2 Hz, 2H), 7.22–7.33 (m, 6H), 7.56 ppm (d, J = 8.0 Hz, 4H); ^{13}C NMR: δ = 15.3, 60.4, 77.2, 79.9, 83.5, 126.5, 127.6, 128.1, 143.4 ppm; IR (neat): $\tilde{\nu}$ = 2110 (C≡C), 3285 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{17}H_{16}O$: C 86.41; H 6.82; found: C 85.97, H 6.67.

Data for 3h: Yield 61 %; a pale yellow oil; ^{1}H NMR: δ = 1.26 (t, J = 7.2 Hz, 3H), 2.31 (s, 6H), 2.83 (s, 1H), 3.52 (q, J = 7.2 Hz, 2H), 7.10 (d, J = 7.6 Hz, 4H), 7.42 ppm (d, J = 7.6 Hz, 4H); ^{13}C NMR: δ = 15.3, 21.0, 60.2, 76.8, 79.6, 83.9, 126.4, 128.8, 137.2, 140.7 ppm; IR (neat): $\tilde{\nu}$ = 2110 (C≡C), 3287 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{19}H_{20}O$: C 86.32, H , 7.63; found: C 85.95, H 7.51.

When phenol and chiral alcohols were used as nucleophiles, the reactions were carried out in $ClCH_2CH_2Cl$ as solvent. A typical experimental procedure for the reaction of **2a** and phenol is as follows. Compound **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) were placed in a 20 mL flask under N_2. Anhydrous $ClCH_2CH_2Cl$ (15 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (0.60 mmol) and phenol (3.00 mmol), the reaction flask was kept at 60 °C for 60 min. The reaction mixture was treated with brine (50 mL) and then extracted with diethyl ether (20 mL × 3). The ether layer was dried over anhydrous $MgSO_4$. For isolation, the extract was concentrated under reduced pressure by an aspirator, and then the residue was purified by HPLC (the eluent: $CHCl_3$) to give **3n** as a pale yellow oil (0.39 mmol, 65 % yield).

Data for 3n: ^{1}H NMR: δ = 2.68 (d, J = 2.0 Hz, 1H), 5.83 (s, 1H), 7.01 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 8.4 Hz, 2H), 7.37–7.43 (m, 3H), 7.61 ppm (d, J = 7.2 Hz, 2H); ^{13}C NMR: δ = 69.7, 76.6, 80.9, 116.1, 121.8, 127.2, 128.7, 128.8, 129.4, 137.4, 157.3 ppm; IR (neat): $\tilde{\nu}$ =

2120 (C≡C), 3289 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{15}H_{12}O$: C 86.51, H 5.81; found: C 86.49, H 5.78.

Data for 3i: Yield 80%; a pale yellow oil; two diastereomers with a ratio of 50:50; ^1H NMR: $\delta = 0.88$ (t, $J = 7.2$ Hz, 3H), 0.92 (d, $J = 7.2$ Hz, 3H), 1.15 (m, 1H), 1.49 (m, 1H), 1.71 (m, 1H), 2.61 (s, 1H), 3.26 and 3.36 (dd each, $J = 8.0$ Hz, 1H), 3.46 and 3.54 (dd each, $J = 8.0$ Hz, 1H), 5.14 (s, 1H), 7.23–7.39 (m, 3H), 7.53 ppm (d, $J = 7.2$ Hz, 2H); ^{13}C NMR: $\delta = 11.2$ and 11.2, 16.6 and 16.6, 26.2 and 26.2, 34.8 and 34.9, 71.2 and 71.3, 73.5 and 73.6, 75.2 and 75.2, 81.9 and 82.0, 127.1, 128.2, 128.4, 138.5 ppm; IR (neat): $\tilde{\nu} = 2114$ (C≡C), 3306 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{14}H_{18}O$: C 83.12, H 8.97; found: C 83.17, H 8.89.

Data for 3j: Yield 92%; a pale yellow oil; two diastereomers with a ratio of 51:49; ^1H NMR: $\delta = 1.31$ (br s, 3H), 2.61 (s, 1H), 3.08 (br s, 1H), 3.51–3.79 (m, 2H), 5.14 and 5.19 (s each, 1H), 7.23–7.44 ppm (m, 10H); ^{13}C NMR: $\delta = 18.4$ and 18.5, 39.8, 71.2, 73.7 and 73.9, 75.5 and 75.6, 81.5 and 81.6, 126.3, 127.1 and 127.1, 127.3, 128.3 and 128.4, 138.1 and 138.1, 144.1 and 144.2 ppm; IR (neat): $\tilde{\nu} = 2114$ (C≡C), 3289 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{18}H_{18}O$: C 86.36, H 7.25; found: C 86.15, H 7.28.

Data for 3k: Yield 69%; a pale yellow oil; two diastereomers with a ratio of 55:45; ^1H NMR: $\delta = 1.44$ and 1.52 (d each, $J = 6.8$ Hz, 3H), 2.54 and 2.61 (d each, $J = 2.0$ Hz, 1H), 4.44 and 5.00 (q each, $J = 6.8$ Hz, 1H), 4.88 and 4.96 (s each, 1H), 7.30–7.47 ppm (m, 10H); ^{13}C NMR: $\delta = 23.7$ and 24.2, 68.2 and 68.5, 74.4 and 74.9, 75.3 and 75.8, 81.8 and 82.8, 126.4 and 126.7, 127.3 and 127.4, 127.7 and 127.8, 128.3, 128.4 and 128.5, 128.6 and 128.6, 138.4 and 138.7, 142.6 and 142.7 ppm; IR (neat): $\tilde{\nu} = 2114$ (C≡C), 3289 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{17}H_{16}O$: C 86.41, H, 6.82; found: C 86.30, H 6.95.

Data for 3l: Yield 64%; a white solid, m.p. 81.5–82.0°C; two diastereomers with a ratio of 70:30; ^1H NMR: $\delta = 1.48$ and 1.60 (d each, $J = 6.6$ Hz, 3H), 1.52 and 1.57 (d each, $J = 6.6$ Hz, 1H), 2.52 and 2.62 (d each, $J = 2.1$ Hz, 1H), 4.91 and 5.01 (d each, $J = 2.1$ Hz, 1H) 7.26–7.87 ppm (m, 12H); ^{13}C NMR: $\delta = 23.7$ and 24.1, 68.4 and 68.7, 74.5 and 75.1, 75.4 and 76.0, 81.8 and 82.8, 124.1 and 124.3, 125.8 and 126.0, 126.0 and 126.1, 127.2 and 127.3, 127.6 and 127.6, 127.8 and 127.8, 128.2 and 128.6, 128.4 and 128.4, 128.0 and 128.3, 128.4 and 128.4, 133.1 and 133.1 ppm; elemental analysis calcd (%) for $C_{21}H_{18}O$: C 88.08, H 6.34; found: C 87.89, H 6.21.

Data for 3m: Yield 71%; a pale yellow oil; two diastereomers with a ratio of 70:30; ^1H NMR: $\delta = 0.49$ and 0.49 (d each, $J = 6.9$ Hz, 1H), 0.83–0.95 (m, 9H), 0.97–1.68 (m, 6H), 2.16–2.38 (m, 2H), 2.54 and 2.57 (d each, $J = 1.8$ Hz, 1H), 3.23 and 3.62 (dt each, $J = 4.2$, 10 Hz, 1H), 5.14 and 5.28 (d each, $J = 1.8$ Hz, 1H) 7.28–7.51 ppm (m, 5H); ^{13}C NMR: $\delta =$ 15.6 and 16.2, 21.1 and 21.1, 22.3 and 22.4, 22.9 and 23.2, 24.9 and 25.2, 31.5 and 31.6, 34.4 and 34.5, 39.7 and 41.1, 48.1 and 48.5, 67.8 and 69.8, 74.3 and 74.7, 76.6 and 78.1, 82.7 and 83.6, 127.2 and 127.5, 128.2 and 128.4, 139.1 and 139.3 ppm; elemental analysis calcd (%) for $C_{19}H_{26}O$: C 84.39, H 9.69; found: C 84.15, H 9.80.

Data for 3p: Yield 81%; a pale yellow oil; ^1H NMR: $\delta = 2.68$ (d, 1H, $J =$ 2.4 Hz), 2.62–2.69 (m, 2H), 3.74–3.82 (m, 1H), 3.86–3.93 (m, 1H), 5.28 (d, $J = 2.4$ Hz, 1H), 7.24–7.55 ppm (m, 5H); ^{13}C NMR: $\delta = 42.6$, 67.9, 71.5, 76.3, 80.8, 127.3, 128.5, 128.6, 137.4 ppm; elemental analysis calcd (%) for $C_{11}H_{11}ClO$: C 67.87, H, 5.70; found: C 67.97, H 5.84.

Data for 3q: Yield 77%; a pale yellow oil; ^1H NMR: $\delta = 2.66$ (d, $J =$ 2.1 Hz, 1H), 4.22 (d, $J = 1.0$ Hz, 1H), 4.23 (d, $J = 1.0$ Hz, 1H), 5.25 (d, $J =$ 2.1 Hz, 1H), 5.40 (d, $J = 1.0$ Hz, 1H), 5.53 (d, $J = 1.0$ Hz, 1H), 7.31–7.55 ppm (m, 5H); ^{13}C NMR: $\delta = 70.3$, 70.4, 76.3, 80.7, 114.4, 127.4, 128.5, 128.7, 137.4, 137.5 ppm; HRMS: m/z calcd for $C_{12}H_{12}ClO$ $[M^+ + H]$: 207.0577; found: 207.0584.

Data for 3r: Yield 50%; a pale yellow oil; ^1H NMR: $\delta = 2.66$ (d, $J =$ 2.0 Hz, 1H), 4.31 (m, 2H), 5.23 (d, $J = 2.0$ Hz, 1H), 6.31 (dt, $J = 6.0$, 16 Hz, 1H), 6.65 (d, $J = 16$ Hz, 1H), 7.21–7.55 ppm (m, 10H); ^{13}C NMR: $\delta = 68.8$, 70.3, 75.6, 81.5, 125.2, 126.4, 127.2, 127.6, 128.3, 128.4, 133.1, 136.4, 138.0 ppm; elemental analysis calcd (%) for $C_{18}H_{16}O$: C 87.06, H, 6.49; found: C 86.76, H 6.59.

Data for 3s: Yield 87%; a pale yellow oil; ^1H NMR: $\delta = 1.87$ (t, $J =$ 2.4 Hz, 3H), 2.64 (d, $J = 2.4$ Hz, 1H), 4.19–4.37 (m, 2H), 5.40 (d, $J =$ 2.4 Hz, 1H), 7.32–7.54 ppm (m, 5H); ^{13}C NMR: $\delta = 3.68$, 56.1, 69.5, 74.5, 75.9, 81.0, 83.2, 127.6, 128.5, 128.6, 137.7 ppm; elemental analysis calcd (%) for $C_{13}H_{12}O$: C 84.75, H 6.57; found: C 84.48, H 6.72.

Data for 3t: Yield 92%; a pale yellow oil; ^1H NMR: $\delta = 2.61$ (d, $J =$ 2.4 Hz, 1H), 5.09 (d, $J = 12$ Hz, 1H), 5.23 (d, $J = 12$ Hz, 1H), 5.89 (d, $J =$ 2.4 Hz, 1H), 7.26–7.37 ppm (m, 4H); ^{13}C NMR: $\delta = 73.0$, 73.1, 74.2, 82.0, 121.1, 121.7, 127.8, 128.3, 138.6, 138.8 ppm; elemental analysis calcd (%) for $C_{10}H_8O$: C 83.31, H 5.59; found: C 82.96, H 5.43.

Data for 3w: Yield 67%; a pale yellow oil; ^1H NMR: $\delta = 2.65$ (s, 1H), 2.68 (s, 1H), 5.93 (s, 1H), 6.10 (s, 1H), 7.48 (d, $J = 3.3$ Hz, 1H), 7.59 (d, $J = 3.3$ Hz, 1H), 7.79–7.85 ppm (m, 4H); ^{13}C NMR: $\delta = 71.8$, 72.0, 75.0, 75.1, 81.0, 81.3, 120.7, 120.8, 126.5, 126.6, 128.1, 133.6, 137.0, 137.1 ppm; HRMS: m/z calcd for $C_{16}H_{10}O$ $[M^+]$: 218.0732; found: 218.0726.

Ruthenium-catalyzed propargylic amination of propargylic alcohols with amines: A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**2a**) with aniline (**5a**) catalyzed by **1a** is described below. Compound **1a** (0.03 mmol) and NH_4BF_4 (0.06 mmol) were placed in a 20 mL flask under N_2. Anhydrous $ClCH_2CH_2Cl$ (18 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (0.60 mmol) and **5a** (3.00 mmol), the reaction flask was kept at 60°C for 1 h. For the isolation of **6a**, the solvent was removed under reduced pressure and the residue was purified by HPLC (the eluent: $CHCl_3$) to give pure **6a** as a yellow oil (95.7 mg, 0.46 mmol, 77%).

***N*-Phenyl-1-phenyl-2-propynylamine (6a)**: ^1H NMR: $\delta = 2.43$ (d, $J = 2$ Hz, 1H), 4.01 (br, 1H), 5.26 (s, 1H), 6.69 (d, $J = 8$ Hz, 2H), 6.77 (d, $J = 7$ Hz, 1H), 7.16–7.21 (m, 2H), 7.30–7.38 (m, 3H), 7.58 ppm (d, $J = 7$ Hz, 2H); ^{13}C NMR: $\delta = 49.7$, 73.1, 82.9, 113.9, 118.7, 127.1, 128.1, 128.7, 129.1, 138.9, 146.2 ppm; IR (KBr): $\tilde{\nu} = 2114$ (C≡C), 3279 (≡CH), 3372 cm^{-1} (NH); elemental analysis calcd (%) for $C_{15}H_{13}N$: C 86.92, H 6.32, N, 6.76; found: C 86.70, H 6.68, N 7.10.

***N*-Phenyl-1-(4-fluorophenyl)-2-propynylamine (6b)**: Yield 68%; a yellow solid, m.p. 47.1–47.9°C; ^1H NMR: $\delta = 2.45$ (d, $J = 2$ Hz, 1H), 4.01 (br, 1H), 5.24 (s, 1H), 6.69 (d, $J = 8$ Hz, 2H), 6.78 (t, $J = 7$ Hz, 1H), 7.04 (t, $J = 8$ Hz, 2H), 7.19 (t, $J = 7$ Hz, 2H), 7.52–7.56 ppm (dd, $J = 8$, 5 Hz, 2H); ^{13}C NMR: $\delta = 49.0$, 73.4, 82.7, 114.0, 115.5 (d, $J = 22$ Hz), 118.8, 128.9 (d, $J = 8$ Hz), 129.2, 134.7 (d, $J = 3$ Hz), 146.0, 162.4 ppm (d, $J = 246$ Hz); IR (KBr): $\tilde{\nu} = 2097$ (C≡C), 3187 (≡CH), 3345 cm^{-1} (NH); elemental analysis calcd (%) for $C_{15}H_{12}FN$: C 79.98, H 5.37, N, 6.22; found: C 80.11, H 5.66, N 6.03.

***N*-Phenyl-1-(4-chlorophenyl)-2-propynylamine (6c)**: Yield 95%; a yellow solid; ^1H NMR: $\delta = 2.47$ (d, $J = 2$ Hz, 1H), 4.03 (br, 1H), 5.25 (d, $J =$ 2 Hz, 1H), 6.69 (d, $J = 8$ Hz, 2H), 6.79 (t, $J = 7$ Hz, 1H), 7.19 (t, $J = 7$ Hz, 2H), 7.34 (d, $J = 8$ Hz, 2H), 7.52 ppm (d, $J = 8$ Hz, 2H); ^{13}C NMR: $\delta =$ 49.3, 73.5, 82.5, 114.0, 118.9, 128.4, 128.8, 129.1, 133.9, 137.4, 145.9 ppm; elemental analysis calcd (%) for $C_{15}H_{12}ClN$: C 74.53, H 5.00, N, 5.79; found: C 74.22, H 4.81, N 5.57.

***N*-Phenyl-1-(4-methylphenyl)-2-propynylamine (6d)**: Yield 82%; a yellow solid, m.p. 68.8–70.0°C; ^1H NMR: $\delta = 2.33$ (s, 3H), 2.42 (d, $J =$ 2 Hz, 1H), 3.98 (br, 1H), 5.22 (d, $J = 2$ Hz, 1H), 6.69 (d, $J = 8$ Hz, 2H), 6.76 (t, $J = 7$ Hz, 1H), 7.16–7.20 (m, 4H), 7.46 ppm (d, $J = 8$ Hz, 2H); ^{13}C NMR: $\delta = 21.1$, 49.4, 72.9, 83.1, 113.9, 118.6, 127.0, 129.1, 129.4, 136.0, 137.9, 146.2 ppm; IR (neat): $\tilde{\nu} = 2110$ (C≡C), 3268 (≡CH), 3386 cm^{-1} (NH); elemental analysis calcd (%) for $C_{16}H_{15}N$: C 86.84, H 6.83, N 6.33; found: C 86.71, H 6.79, N 6.11.

***N*-Phenyl-1-(4-methoxyphenyl)-2-propynylamine (6e)**: Yield 59%; a pale yellow oil; ^1H NMR: $\delta = 2.45$ (d, $J = 2$ Hz, 1H), 3.78 (s, 3H), 3.90 (br, 1H), 5.22 (d, $J = 2$ Hz, 1H), 6.71 (d, $J = 8$ Hz, 2H), 6.77 (t, $J = 8$ Hz, 1H), 6.90 (d, $J = 9$ Hz, 2H), 7.20 (t, $J = 8$ Hz, 2H), 7.50 ppm (d, $J = 8$ Hz, 2H); ^{13}C NMR: $\delta = 49.1$, 55.2, 72.9, 83.1, 113.9, 114.0, 118.6, 128.4, 129.1, 131.0, 146.2, 159.4 ppm; IR (neat): $\tilde{\nu} = 2114$ (C≡C), 3287 (≡CH), 3395 cm^{-1} (NH); HRMS: m/z calcd for $C_{16}H_{15}NO$ $[M^+]$: 237.11536; found: 237.11618.

***N*-Phenyl-1-(1-naphthyl)-2-propynylamine (6f)**: Yield 86%; a pale yellow oil; ^1H NMR: $\delta = 2.49$ (d, $J = 2$ Hz, 1H), 4.08 (br, 1H), 5.88 (s, 1H), 6.72 (d, $J = 8$ Hz, 2H), 6.78 (t, $J = 7$ Hz, 1H), 7.19 (t, $J = 8$ Hz, 2H), 7.42–7.48 (m, 3H), 7.79–7.85 (m, 2H), 7.94 (d, $J = 7$ Hz, 1H), 8.05 ppm (m, 1H);

^{13}C NMR: δ = 47.3, 73.6, 82.6, 113.6, 118.5, 123.3, 125.3, 125.3, 125.9, 126.6, 128.8, 129.2, 129.2, 130.5, 133.6, 133.9, 146.2 ppm; IR (neat): $\tilde{\nu}$ = 2114 (C≡*C*), 3289 (≡CH), 3397 cm^{-1} (NH); HRMS: *m*/*z* calcd for $C_{19}H_{15}N$ [M^+] 257.12045; found: 257.12069.

***N*-Phenyl-1-cyclohexyl-2-propynylamine (6g)**: Yield 71%; a yellow solid, m.p. 75.5–76.5°C; ^{1}H NMR: δ = 1.18–1.31 (m, 5H), 1.67–1.90 (m, 6H), 2.21 (d, *J* = 2 Hz, 1H), 3.75 (br s, 1H), 3.94 (dd, *J* = 5 and 2 Hz, 1H), 6.68 (d, *J* = 8 Hz, 2H), 6.75 (t, *J* = 8 Hz, 1H), 7.19 ppm (t, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 25.8, 26.0, 26.2, 28.4, 29.7, 41.9, 51.0, 71.6, 83.4, 113.8, 118.2, 129.1, 146.7 ppm; IR (KBr): $\tilde{\nu}$ = 2101 (C≡C), 3260 (≡CH), 3384 cm^{-1} (NH); elemental analysis calcd (%) for $C_{15}H_{19}N$: C 84.46, H 8.98, N, 6.57; found: C 84.21, H 8.79, N 6.83.

***N*-(2-Trifluoromethylphenyl)-1-phenyl-2-propynylamine (6h)**: Yield 68%; a pale yellow oil; ^{1}H NMR: δ = 2.49 (d, *J* = 2 Hz, 1H), 4.77 (s, 1H), 5.34 (s, 1H), 6.79 (t, *J* = 8 Hz, 1H), 6.90 (d, *J* = 8 Hz, 1H), 7.31–7.41 (m, 4H), 7.47 (d, *J* = 8 Hz, 1H), 7.58 ppm (d, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 49.3, 73.7, 82.1, 113.4, 114.5 (q, *J* = 29 Hz), 117.4, 124.9 (q, *J* = 271 Hz), 126.6 (q, *J* = 5 Hz), 127.0, 128.4, 129.0, 133.0, 138.2, 143.7 ppm; IR (neat): $\tilde{\nu}$ = 2118 (C≡C), 3297 (≡CH), 3465 cm^{-1} (NH); HRMS: *m*/*z* calcd for $C_{16}H_{12}F_3N$ [M^+]: 275.09216; found: 275.09223.

Methyl 2-(1-phenyl-2-propynylamino)benzoate (6i): Yield 82%; a yellow solid, m.p. 72.0–72.5°C; ^{1}H NMR: δ = 2.47 (d, *J* = 2 Hz, 1H), 3.80 (s, 3H), 3.90 (br s, 1H), 5.36 (dd, *J* = 6, 2 Hz, 1H), 6.66 (t, *J* = 8 Hz, 1H), 6.82 (d, *J* = 9 Hz, 1H), 7.29–7.39 (m, 3H), 7.58 (d, *J* = 8 Hz, 2H), 7.93 (dd, *J* = 8, 2 Hz, 1H), 8.26 ppm (d, *J* = 6 Hz, 1H); ^{13}C NMR: δ = 48.6, 51.7, 73.1, 82.6, 111.1, 112.5, 116.0, 127.0, 128.2, 129.0, 131.6, 134.5, 138.6, 149.1, 168.9 ppm; IR (KBr): $\tilde{\nu}$ = 2123 (C≡C), 3266 (≡CH), 3360 cm^{-1} (NH); HRMS: *m*/*z* calcd for $C_{17}H_{16}NO_2$ [M^++H]: 266.11810; found: 266.11791.

***N*-(4-Nitrophenyl)-1-phenyl-2-propynylamine (6j)**: Yield 88%; a yellow solid, m.p. 122.3–123.8°C; ^{1}H NMR: δ = 2.55 (d, *J* = 2 Hz, 1H), 4.99 (br s, 1H), 5.37 (s, 1H), 6.67 (d, *J* = 9 Hz, 2H), 7.34–7.43 (m, 3H), 7.57 (d, *J* = 8 H, 2Hz), 8.07 ppm (d, *J* = 9 Hz, 2H); IR (neat): $\tilde{\nu}$ = 2116 (C≡C), 3376 (≡CH), 3407 cm^{-1} (NH); elemental analysis calcd (%) for $C_{15}H_{12}N_2O_2$: C 71.42, H 4.79, N 11.10; found: C 70.99, H 4.86, N 10.91.

***N*-(4-Methylphenyl)-1-phenyl-2-propynylamine (6k)**: Yield 64%; a yellow oil; ^{1}H NMR: δ = 2.24 (s, 3H), 2.44 (s, 1H), 3.81 (br, 1H), 5.24 (s, 1H), 6.64 (d, *J* = 8 Hz, 2H), 7.01 (d, *J* = 8 Hz, 2H), 7.29–7.38 (m, 3H), 7.59 ppm (d, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 20.4, 50.1, 73.1, 83.0, 114.2, 127.2, 128.0, 128.1, 128.7, 129.6, 139.0, 143.8 ppm; IR (neat): $\tilde{\nu}$ = 2112 (C≡C), 3289 (≡CH), 3403 cm^{-1} (NH); elemental analysis calcd (%) for $C_{16}H_{15}N$: C 86.84, H 6.83, N 6.33; found: C 86.64, H, 6.58, N 6.03.

9-(1-Phenyl-2-propynyl)-9*H*-carbazole (6l): Yield 83%; a pale purple solid, m.p. 97.6–98.7°C; ^{1}H NMR: δ = 2.54 (s, 1H), 6.74 (s, 1H), 7.18–7.21 (m, 5H), 7.30–7.38 (m, 6H), 8.06 ppm (d, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 48.7, 75.3, 79.0, 110.0, 119.6, 120.3, 123.5, 125.7, 126.4, 128.1, 128.6, 136.2, 139.4 ppm; IR (KBr): $\tilde{\nu}$ = 2124 (C≡C), 3289 cm^{-1} (≡CH); elemental analysis calcd (%) for $C_{21}H_{15}N$: C 89.65, H 5.37, N 4.98; found: C 89.35, H 5.40, N 5.00.

***N*-Methyl-*N*-phenyl-1-phenyl-2-propynylamine (6m)**: Yield 41%; a pale yellow oil; ^{1}H NMR: δ = 2.52 (d, *J* = 2 Hz, 1H), 2.70 (s, 3H), 5.81 (s, 1H), 6.86 (t, *J* = 8 Hz, 1H), 6.99 (d, *J* = 8 Hz, 2H), 7.24–7.39 (m, 5H), 7.58 ppm (d, 2H, *J* = 8 Hz); ^{13}C NMR: δ = 33.6, 56.3, 74.8, 79.9, 115.2, 118.9, 127.5, 127.8, 128.4, 129.2, 137.8, 150.0 ppm; IR (neat): $\tilde{\nu}$ = 2110 (C≡C), 3291 cm^{-1} (≡CH); HRMS: *m*/*z* calcd for $C_{16}H_{15}N$ [M^+]: 221.12045; found: 221.12048.

***N*-(4-Chlorophenyl)-1-phenyl-2-propynylamine**: Yield 93%; a yellow solid; ^{1}H NMR: δ = 2.48 (d, *J* = 2 Hz, 1H), 4.06 (br, 1H), 5.24 (d, *J* = 2 Hz, 1H), 6.64 (d, *J* = 8 Hz, 2H), 7.12 (d, *J* = 8 Hz, 2H), 7.37 (m, 3H), 7.57 ppm (d, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 50.0, 73.4, 82.5, 115.1, 123.4, 127.1, 128.3, 128.8, 128.9, 138.4, 144.7 ppm; elemental analysis calcd (%) for $C_{15}H_{12}ClN$: C 74.53, H 5.00, N 5.79; found: C 74.31, H 4.96, N 5.39.

***N*-(1-Phenyl-2-propynyl)acetamide (8a)**: Yield 79%; a white solid, m.p. 84.0–85.6°C; ^{1}H NMR: δ = 1.96 (s, 3H), 2.47 (d, *J* = 2.2 Hz, 1H), 5.98 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 7.27–7.36 (m, 3H), 7.58 ppm (d, *J* = 8.0 Hz, 2H); ^{13}C NMR: δ = 22.9, 44.3, 72.8, 81.7, 126.9, 128.0, 128.6, 138.2, 169.1 ppm; IR (neat): $\tilde{\nu}$ = 2114 (C≡C), 3293 (≡CH), 3449 cm^{-1} (NH); elemental analysis calcd (%) for $C_{11}H_{11}NO$: C 76.28, H 6.40, N 8.09; found: C 76.66, H 6.36, N 7.70.

Data for 8b: Yield 62%; a white solid, m.p. 118.5–118.8°C; ^{1}H NMR: δ = 2.01 (s, 3H), 2.50 (d, *J* = 2.0 Hz, 1H), 5.97 (dd, *J* = 5.8, 2.0 Hz, 1H), 6.08 (d, *J* = 5.8 Hz, 1H), 7.01 (t, *J* = 5.8 Hz, 2H), 7.46 ppm (m, 2H); ^{13}C NMR: δ = 23.2, 43.9, 73.2, 81.4, 115.5 (d, *J* = 23 Hz), 128.8 (d, *J* = 8 Hz), 134.1, 164.9 ppm (d, *J* = 256 Hz); elemental analysis calcd (%) for $C_{11}H_{10}FNO$: C 69.10, H 5.27, N 7.33; found: C 69.23, H 5.27, N 7.36.

Data for 8c: Yield 50%; a pale yellow solid, m.p. 118.8–119.8°C; ^{1}H NMR: δ = 2.03 (s, 3H), 2.51 (s, 1H), 6.00 (br s, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.43 ppm (d, *J* = 8.6 Hz, 2H); ^{13}C NMR: δ = 23.2, 43.9, 73.4, 81.2, 128.3, 128.7, 134.0, 136.7, 168.8 ppm; elemental analysis calcd (%) for $C_{11}H_{11}ClNO$: C 63.62, H 4.85, N 6.75; found: C 63.45, H 4.91, N 6.55.

Data for 8d: Yield 58%; a white solid, m.p. 98.8–99.9°C; ^{1}H NMR: δ = 1.96 (s, 3H), 2.32 (s, 3H), 2.45 (d, *J* = 2.4 Hz, 1H), 5.90 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.54 (br d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.35 ppm (d, 2H, *J* = 7.8 Hz); ^{13}C NMR: δ = 21.1, 23.0, 44.2, 72.6, 81.9, 126.7, 129.1, 135.2, 137.7, 168.8 ppm; elemental analysis calcd (%) for $C_{12}H_{13}NO$: C 76.98, H 7.00, N 7.48; found: C 76.70, H, 6.97, N, 7.36.

Data for 8e: Yield 70%; a pale yellow solid, m.p. 129.8–130.2°C; ^{1}H NMR: δ = 1.97 (s, 3H), 2.47 (d, *J* = 2.2 Hz, 1H), 3.78 (s, 3H), 5.91 (dd, *J* = 6.2, 2.2 Hz, 1H), 6.47 (d, *J* = 6.2 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.39 ppm (d, *J* = 8.6 Hz, 2H); ^{13}C NMR: δ = 23.1, 43.9, 55.2, 72.6, 81.9, 113.8, 128.1, 130.3, 159.2, 168.8 ppm; elemental analysis calcd (%) for $C_{12}H_{13}NO_2$: C 70.92, H 6.45, N 6.89; found: C 70.71, H 6.44, N 6.90.

Data for 8f: Yield 42%; a white solid, m.p. 144.0–145.0°C; ^{1}H NMR: δ = 1.99 (s, 3H), 2.53 (d, *J* = 2.4 Hz, 1H), 6.13 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.49 (d, *J* = 8.6 Hz, 1H), 7.44–7.53 (m, 3H), 7.77–7.82 (m, 3H), 7.96 ppm (m, 1H); ^{13}C NMR: δ = 23.1, 44.6, 73.2, 81.6, 124.7, 125.8, 126.2, 127.5, 127.9, 128.5, 132.8, 132.9, 135.3, 168.9 ppm; elemental analysis calcd (%) for $C_{15}H_{13}NO$: C 80.69, H 5.87, N 6.27; found: C 80.42, H 5.71, N 6.09.

Data for 8g: Yield 41%; a yellow solid, m.p. 142.0–143.4°C; ^{1}H NMR: δ = 1.90 (s, 3H), 2.33 (d, *J* = 2.4 Hz, 1H), 5.23–5.30 (ddd, *J* = 9.2, 7.3, 2.4 Hz, 1H), 5.96 (d, *J* = 9.2 Hz, 1H), 6.23 (d, *J* = 7.3 Hz, 1H), 7.19–7.40 ppm (m, 10H); ^{13}C NMR: δ = 23.1, 40.9, 71.5, 82.5, 124.3, 127.5, 127.7, 128.0, 128.2, 129.4, 138.1, 141.1, 144.6, 168.4 ppm; elemental analysis calcd (%) for $C_{19}H_{17}NO$: C 82.88, H 6.22, N 5.09; found: C 82.63, H 6.40, N 4.99.

Data for 8h: Yield 72%; a yellow solid, m.p. 117.2–118.8°C; ^{1}H NMR: δ = 1.13 (d, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 7.2 Hz, 3H), 2.35 (sept, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 2.2 Hz, 1H), 6.00 (dd, *J* = 2.2, 8.4 Hz, 1H), 6.16 (d, *J* = 8.4 Hz, 1H), 7.29–7.37 (m, 3H), 7.46 ppm (m, 2H); ^{13}C NMR: δ = 19.3, 19.5, 35.4, 44.2, 72.9, 81.8, 126.7, 127.9, 128.5, 138.3, 175.5 ppm; elemental analysis calcd (%) for $C_{13}H_{15}NO$: C 77.58, H 7.51, N 6.96; found: C 77.29, H 7.38, N 6.88.

Data for 8i: Yield 56%; a pale yellow solid, m.p. 145.5–147.1°C; ^{1}H NMR: δ = 1.20 (m, 3H), 1.39 (m, 2H), 1.67–1.91 (m, 6H), 2.05–2.16 (m, 1H), 2.47 (s, 1H), 6.04 (br, 1H), 7.29 (m, 3H), 7.47 ppm (m, 2H); ^{13}C NMR: δ = 25.7, 29.4, 29.6, 44.1, 45.2, 72.8, 81.9, 126.7, 128.0, 128.5, 138.4, 174.5 ppm; elemental analysis calcd (%) for $C_{16}H_{19}NO$: C 79.63, H 7.94, N 5.80; found: C 79.34, H, 7.87, N 5.72.

Data for 8j: Yield 71%; a white solid, m.p. 103.4–104.1°C; ^{1}H NMR: δ = 2.48 (d, *J* = 2.4 Hz, 1H), 5.62 (dd, *J* = 2.4, 10.2 Hz, 1H), 6.06 (dd, *J* = 9.7, 17 Hz, 1H), 6.13 (d, *J* = 9.7 Hz, 1H), 6.27 (d, *J* = 17 Hz, 1H), 6.56 (d, *J* = 10.2 Hz, 1H), 7.28–7.37 (m, 3H), 7.47–7.51 ppm (m, 2H); ^{13}C NMR: δ = 44.5, 73.1, 81.5, 126.9, 127.4, 128.1, 128.6, 130.0, 137.9, 164.2 ppm; elemental analysis calcd (%) for $C_{12}H_{11}NO$: C 77.81, H 5.99, N 7.56; found: C 77.86, H 6.01, N 7.38.

Data for 8k: Yield 71%; a white solid; ^{1}H NMR: δ = 2.53 (d, *J* = 2 Hz, 1H), 6.86 (dd, *J* = 2, 8 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 7.25–7.79 (m, 8H), 7.58 ppm (d, *J* = 8 Hz, 2H); ^{13}C NMR: δ = 44.5, 73.1, 81.5, 126.9, 127.4, 128.1, 128.6, 130.0, 137.9, 164.2 ppm; IR (neat): $\tilde{\nu}$ = 2123 (C≡C), 3279 (≡CH), 3326 cm^{-1} (NH); HRMS: *m*/*z* calcd for $C_{16}H_{14}NO$ [M^++H]: 236.10754; found: 236.10770.

Data for 8l: Yield 61%; a white solid, m.p. 138.8–139.9°C; ^{1}H NMR: δ = 2.52 (d, *J* = 2.2 Hz, 1H), 6.17 (dd, *J* = 2.2, 8.1 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 7.31 (m, 5H), 7.54 (d, *J* = 6.2 Hz, 2H), 7.68 ppm (d, *J* = 8.1 Hz, 2H);

^{13}C NMR: δ=45.1, 73.4, 81.4, 127.0, 128.2, 128.5, 128.7, 131.8, 137.8, 137.9, 165.1 ppm; elemental analysis calcd (%) for $C_{16}H_{12}ClNO$: C 71.25, H 4.48, N 5.19; found: C 71.22, H 4.67, N 4.96.

Data for 8m: Yield 67%; a white solid, m.p. 138.9–139.9°C; ^{1}H NMR: δ=2.35 (s, 3H), 2.49 (d, J=2.4 Hz, 1H), 6.19 (dd, J=2.4, 8.6 Hz, 1H), 6.87 (d, J=8.4 Hz, 1H), 7.14 (d, J=7.8 Hz, 2H), 7.23–7.35 (m, 3H), 7.53 (d, J=6.2 Hz, 2H), 7.65 ppm (d, J=7.8 Hz, 2H); ^{13}C NMR: δ=21.4, 44.8, 73.1, 81.7, 126.9, 127.0, 128.0, 128.5, 129.0, 130.6, 138.1, 142.0, 166.0 ppm; elemental analysis calcd (%) for $C_{17}H_{15}NO$: C 81.90, H 6.06, N 5.62; found: C 81.88, H 6.15, N 5.41.

Data for 8n: Yield 64%; a pale yellow oil; ^{1}H NMR: δ=2.61 and 2.69 (s each, 1H), 2.78 and 2.89 (s each, 3H), 5.87 (br s, 1H), 7.03–7.61 ppm (m, 10H); GCMS: m/z (%): 249 (20) [M^+], 248 (28) [M^+-1], 220 (15), 144 (14), 118 (47), 115 (55) [PhCHCCH$^+$], 105 (100) [PhCO$^+$], 89 (9), 77 (84) [Ph$^+$]; IR (neat): $\tilde{\nu}$=1636 (C=O), 2116 (C≡C), 3289 cm^{-1} (≡*CH*); elemental analysis calcd (%) for $C_{17}H_{15}NO$: C 81.90, H 6.06, N, 5.62; found: C 82.27, H 6.13, N 5.64.

Data for 8o: Yield 64%; a yellow oil; ^{1}H NMR: δ=2.15 (s, 3H), 2.53 (d, J=2.7 Hz, 1H), 2.82 (s, 3H), 6.91 (d, J=2.7 Hz, 1H), 7.27–7.39 (m, 3H), 7.42–7.48 ppm (m, 2H); ^{13}C NMR: δ=21.8, 31.1, 48.1, 74.3, 79.6, 127.2, 128.3, 128.6, 136.2, 170.1 ppm; HRMS: m/z calcd for $C_{12}H_{13}NO$ [M^+]: 187.0997; found: 187.0999.

Data for 8p: Yield 63%; a white solid, m.p. 78.2–78.8°C; ^{1}H NMR: δ=2.65 (d, J=2.2 Hz, 1H), 2.98 (s, 3H), 5.27 (d, J=2.2 H, 1Hz), 5.27 (dd, J=2.2, 8.4 Hz, 1H), 7.31–7.39 (m, 3H), 7.51 ppm (m, 2H); ^{13}C NMR: δ=41.5, 48.8, 75.2, 80.9, 127.1, 128.5, 128.7, 136.5 ppm; elemental analysis calcd (%) for $C_{10}H_{11}NO_2S$: C 57.39, H 5.30, N 6.69; found: C 57.44, H 5.35, N 6.58.

Data for 8q: Yield 52%; a white solid, m.p. 131.0–132.0°C; ^{1}H NMR: δ=2.29 (s, 1H), 2.40 (s, 3H), 5.30 (br s, 2H), 7.23–7.27 (m, 5H), 7.42 (d, J=8.1 Hz, 2H), 7.74 ppm (d, J=8.1 Hz, 2H); ^{13}C NMR: δ=21.5, 48.8, 74.7, 80.3, 127.1, 127.3, 128.4, 128.6, 129.4, 136.9, 137.1, 143.5 ppm; elemental analysis calcd (%) for $C_{16}H_{15}NO_2S$: C 67.34, H 5.30; found: C 67.07, H 5.25.

Data for 8r: Yield 78%; a yellow oil; ^{1}H NMR: δ=2.58 (d, J=2.4 Hz, 1H), 2.88–3.37 (m, 4H), 5.86 (d, J=2.4 Hz, 1H), 7.27–7.48 ppm (m, 5H); ^{13}C NMR: δ=36.1, 36.2, 46.7, 74.4, 78.3, 127.0, 128.1, 128.5, 135.4, 166.3 ppm; HRMS: m/z calcd for $C_{12}H_{12}NO$ [M^++H]: 186.0919; found: 186.0921.

Data for 8s: Yield 74%; a yellow oil; ^{1}H NMR: δ=1.86–2.03 (m, 2H), 2.40–2.46 (m, 2H), 2.55 (d, J=2.2 Hz, 1H), 3.05 (m, 1H), 3.55 (m, 1H), 6.31 (d, J=2.2 Hz, 1H), 7.28–7.38 (m, 3H), 7.46 ppm (d, J=6.2 Hz, 2H); ^{13}C NMR: δ=20.4, 21.7, 30.9, 41.4, 68.7, 76.1, 126.8, 127.4, 127.7, 127.8, 172.2 ppm; HRMS: m/z calcd for $C_{13}H_{13}NO$ [M^+]: 199.0997; found: 199.0998.

Data for 8t: Yield 18%; a yellow oil; ^{1}H NMR: δ=1.67–1.79 (m, 4H), 2.47 (m, 3H), 2.84 (m, 1H), 3.43 (m, 1H), 7.02 (s, 1H), 7.29–7.37 (m, 3H), 7.47 ppm (d, J=6.5 Hz, 2H); ^{13}C NMR: δ=21.2, 23.1, 32.5, 42.5, 47.8, 74.3, 79.6, 127.4, 127.8, 128.4, 136.2, 169.2 ppm; HRMS: m/z calcd for $C_{14}H_{15}NO$ [M^+]: 213.1154; found: 213.1151.

Data for 10a: Yield 84%; a white solid, m.p. 145.6–146.8°C; ^{1}H NMR: δ=2.42 (dd, J=3.0, 6.0 Hz, 1H), 4.65 (dd, J=3.0, 18 Hz, 1H), 7.18–7.84 ppm (m, 15H); ^{31}P NMR: δ=29.9 ppm; IR (neat): $\tilde{\nu}$=1191 (P=O), 2116 (C≡C), 3295 cm^{-1} (≡CH); HRMS: m/z calcd for $C_{21}H_{18}OP$ [M^++H]: 317.1094; found: 317.1087.

Data for 10b: Yield 81%; a white solid, m.p. 154.8–156.4°C; ^{1}H NMR: δ=2.42 (dd, J=2.6, 6.0 Hz, 1H), 4.59 (dd, J=2.6, 18.6 Hz, 1H), 6.86 (t, J=8.6 Hz, 2H), 7.18–7.25 (m, 2H), 7.43–7.25 (m, 6H), 7.73–7.83 ppm (m, 4H); elemental analysis calcd (%) for $C_{21}H_{16}FOP$: C 75.44, H 4.82; found: C 75.04, H 4.85.

Data for 10c: Yield 74%; a white solid, m.p. 150.2–151.8°C; ^{1}H NMR: δ=2.42 (dd, J=2.6, 5.4 Hz, 1H), 4.6 (dd, J=2.6, 19.2 Hz, 1H), 7.16 (s, 4H), 7.41–7.55 (m, 6H), 7.74–7.82 ppm (m, 4H); elemental analysis calcd (%) for $C_{21}H_{16}ClOP$: C 71.90, H 4.60; found: C 72.05, H 4.64.

Data for 10d: Yield 84%; a white solid, m.p. 148.9–150.6°C; ^{1}H NMR: δ=2.28 (s, 3H), 2.39 (dd, J=2.7, 5.6 Hz, 1H), 4.60 (dd, J=2.7, 18.8 Hz, 1H), 6.99–7.12 (m, 4H), 7.41–7.56 (m, 6H), 7.73–7.85 ppm (m, 4H); elemental analysis calcd (%) for $C_{22}H_{19}P$: C 79.98, H 5.80; found: C 79.85, H 5.69.

Data for 10e: Yield 78%; a white solid, m.p. 160.0–160.8°C; ^{1}H NMR: δ=2.22 (s, 3H), 2.40 (dd, J=2.7, 5.6 Hz, 1H), 4.60 (dd, J=2.7, 18.5 Hz, 1H), 6.98–7.10 (m, 4H), 7.37–7.56 (m, 6H), 7.72–7.85 ppm (m, 4H); elemental analysis calcd (%) for $C_{22}H_{19}OP$: C 79.98; H 5.80; found: C 79.95, H 5.77.

Data for 10f: Yield 87%; a brownish white solid, m.p. 182.4–184.1°C; ^{1}H NMR: δ=2.14 (s, 3H), 2.31 (dd, J=2.7, 5.6 Hz, 1H), 4.88 (dd, J=2.7, 17.1 Hz, 1H), 7.04–7.16 (m, 3H), 7.26–7.29 (m, 1H), 7.34–7.51 (m, 3H), 7.56–7.70 (m, 3H), 7.81–7.88 ppm (m, 4H); elemental analysis calcd (%) for $C_{22}H_{19}OP$: C 79.98, H 5.80; found: C 80.25, H 5.79.

Data for 10g: Yield 88%; a pale yellow solid, m.p. 170.6–171.6°C; ^{1}H NMR: δ=2.39 (dd, J=2.6, 5.4 Hz, 1H), 3.74 (s, 3H), 4.60 (dd, J=2.6, 18.5 Hz, 1H), 6.73–6.80 (m, 2H), 7.12 (d, J=7.0 Hz, 2H), 7.41–7.57 (m, 6H), 7.73–7.84 ppm (m, 4H); elemental analysis calcd (%) for $C_{22}H_{19}O_2P$: C 76.29, H 5.53; found: C 76.12, H 5.56.

Data for 10h: Yield 90%; a white solid, m.p. 153.8–154.6°C. ^{1}H NMR: δ=2.46 (dd, J=2.7, 5.4 Hz, 1H), 4.77–4.85 (dd, J=2.7, 18.9 Hz, 1H), 7.41–7.46 (m, 8H), 7.67–7.82 ppm (m, 9H); HRMS: m/z calcd for $C_{25}H_{19}OP$ [M^+]: 366.1174; found: 366.1169.

Data for 10i: Yield 67%; a yellow viscous oil; ^{1}H NMR: δ=2.28 (dd, J=5.4, 2.7 Hz, 1H), 4.17–4.27 (dd, J=2.7, 18 Hz, 1H), 6.13 (dd, J=6.9, 18 Hz, 1H), 6.96–7.85 ppm (m, 20H); HRMS: m/z calcd for $C_{29}H_{23}OP$ [M^+]: 418.1487; found: 418.1489.

Data for 10j: Yield 90%; a white solid, m.p. 198.2–199.8°C; ^{1}H NMR: δ=2.91 (dd, J=1.0, 5.4 Hz, 1H), 7.14–7.27 (m, 10H), 7.36–7.41 (m, 2H), 7.65–7.78 ppm (m, 8H); elemental analysis calcd (%) for $C_{27}H_{21}OP$: C 82.64, H 5.39; found: C 82.34, H 5.46.

Data for 10k: Yield 96%; a white solid, m.p. >250°C; ^{1}H NMR: δ=2.27 (s, 6H), 2.85 (dd, J=1.0, 5.4 Hz, 1H), 7.00 (d, J=8.4 Hz, 4H), 7.24–7.31 (m, 4H), 7.40–7.45 (m, 2H), 7.59 (d, J=8.4 Hz, 4H), 7.67–7.73 ppm (m, 4H); HRMS: m/z calcd for $C_{29}H_{26}OP$ [M^++H]: 421.1721; found: 421.1705.

Preparation of [(Cp*)RuCl(μ$_2$-SMe)$_2$Ru(Cp*)(C=C=C(*p*-tol)$_2$)]BF$_4$·CH$_2$Cl$_2$ (11a·CH$_2$Cl$_2$):[15] Compound **1a** (144 mg, 0.20 mmol) and NH_4BF_4 (22 mg, 0.20 mmol) were placed in a 20 mL flask under N_2. Anhydrous EtOH (10 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2f** (47 mg, 0.20 mmol), the reaction flask was kept at room temperature for 1 h. A purple solid precipitated was filtered off, washed with *n*-hexane, and recrystallized from CH_2Cl_2/*n*-hexane to give black crystals of **11a**·CH_2Cl_2 (167 mg,0.168 mmol, 84%); ^{1}H NMR: δ=1.66 (s, 15H), 1.84 (s, 15H), 2.33 (s, 6H), 2.66 (s, 6H), 7.19 (d, J=7.6 Hz, 4H), 7.51 ppm (d, J=7.6 Hz, 4H); ^{13}C NMR: δ=10.4, 10.7, 19.6, 22.0, 98.8, 104.5, 129.9, 132.1, 140.4, 144.5, 162.2, 182.6, 296.6 ppm. IR (KBr): $\tilde{\nu}$=1946 cm^{-1} (C=C=C); elemental analysis calcd (%) for $C_{39}H_{50}BClF_4Ru_2S_2\cdot CH_2Cl_2$: C 48.42, H 5.28; found: C 48.29, H 5.31.

Preparation of [(Cp*)RuCl(μ$_2$-SMe)$_2$Ru(Cp*)(=C=C=CHPh)]BF$_4$ (11b): A typical experimental procedure for the preparation of [(Cp*)RuCl(μ$_2$-SMe)$_2$Ru(Cp*)(C=C=CHPh)]BF_4 (**11b**) is described below. Comopund **1a** (510 mg, 0.80 mmol), NH_4BF_4 (109 mg, 1.04 mmol), and $MgSO_4$ (1 g) were placed in a 200 mL flask under N_2. Anhydrous THF (100 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (219 mg, 1.66 mmol), the reaction flask was kept at room temperature for 30 min. Then, the solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/diethyl ether to give black crystals of **11b** (378 mg, 0.467 mmol, 58%). ^{1}H NMR: δ=1.66 (s, 15H), 1.85 (s, 15H), 2.73 (s, 6H), 7.39 (t, J=7.5 Hz, 2H), 7.66 (t, J=7.5 Hz, 1H), 7.72 (d, J=7.5 Hz, 2H) 8.89 ppm (s, 1H); ^{13}C NMR: δ=10.4, 10.6, 20.1, 99.4, 105.6, 130.2, 132.4, 134.0, 142.6, 151.2, 198.0, 319.7 ppm; IR (KBr): $\tilde{\nu}$=1945 cm^{-1} (C=C=C); elemental analysis calcd (%) for $C_{31}H_{42}BClF_4Ru_2S_2$: C 46.36, H 5.27; found: C 46.00, H 5.15.

X-ray crystallographic data: CCDC 247325 (**8j**), CCDC 247326 (**8q**), CCDC 247327 (**10a**) and CCDC 247328 (**10b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

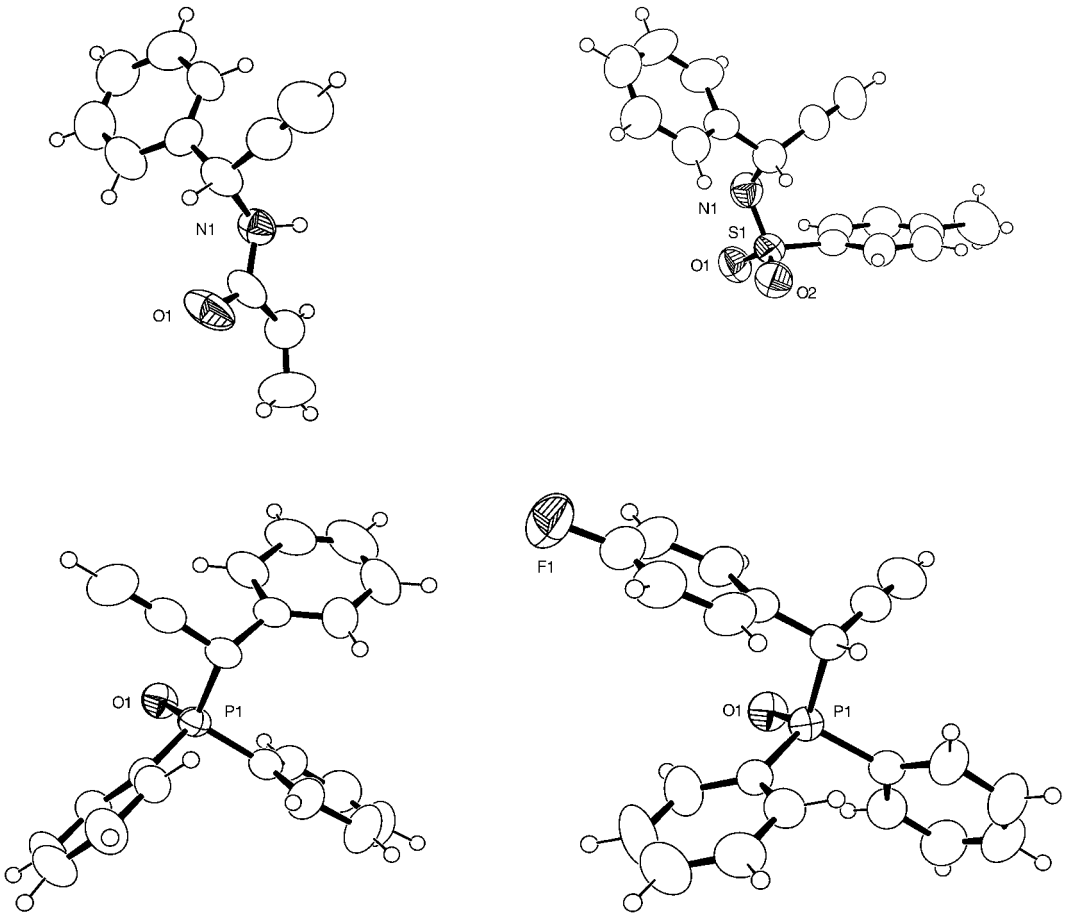


Figure 3. ORTEP drawings of **8j** (top left), **8q** (top right), **10a** (bottom left), and **10b** (bottom right) with 50% probability ellipsoids.

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. ORTEP drawings of **8j**, **8q**, **10a**, and **10b** are shown in Figure 3.

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