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Cobalt(III)–Catalyzed C–H Activation: Counter Anion Triggered Desilylative Direct *ortho*-Vinylation of Secondary Benzamides

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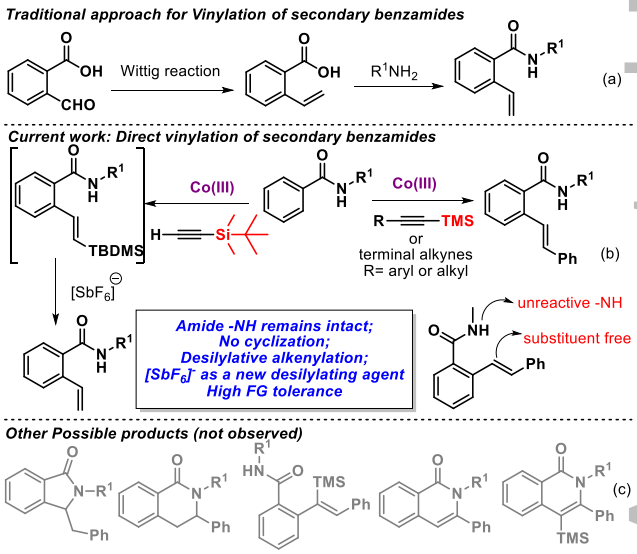
Abstract. A Co(III)-catalyzed counter anion triggered desilylative direct *ortho*-vinylation of secondary benzamides is reported. The reaction furnishes the alkenylated product, exclusively, and no formation of the possible cyclic products was observed. Mechanistic studies suggest that the counter anion, $[SbF_6]^-$, plays a crucial role in the desilylation. The utility of alkynylsilanes instead of terminal alkynes turned out to be a potential and practical approach to obtain the corresponding vinylated products. The developed methodology is compatible with a variety of functional groups.

Keywords: Cobalt; amides; alkynylsilane; desilylation; alkenylation; C-H activation

Introduction

Alkene is an important functional group that can easily be transformed into a variety of functional groups. Development of a direct alkenylation method employing directing group strategy is attractive as well as atom-economical.[1] Alkenylation is achieved by employing either alkene[2] or alkyne[3] as coupling partner using high-valent metal catalysts. In these alkenylation reactions, use of alkynes as coupling partners offers a major advantage as alkynes can undergo a redox neutral process which does not require external oxidant. There are many reports on the use of internal alkynes to obtain internal alkenes,[3] whereas the utility of terminal alkynes for similar reactions are limited.[4] Generally, terminal alkynes are less compatible with many of the C-H activation reactions.[3] Yu and Cheng reported the *ortho*-alkenylation of 2-phenyl pyridine derivatives using terminal alkynes as coupling partners.[4a] The amide is a weak coordinating group, which has been well explored as a directing group in C-H activation reactions such as alkenylation,[2,3] annulations,[5] etc.[6] Besides, secondary benzamides have a free-NH group, which are well known to form cyclized products in the directed alkenylation reactions with alkynes.[5] However, under similar reaction conditions, it is challenging to terminate the reaction without cyclization to yield exclusively the olefin derivatives. Traditional vinylation methods of

Scheme 1. Direct vinylation of secondary benzamides



benzamides involve a multistep sequence of Wittig reaction followed by coupling the acid with an amine (Scheme 1a). Vinyl acetate, vinyl carboxylic acid or vinyl stannane have been employed for the direct vinylation reactions of benzamides in the presence of various directing groups, which invariably require an external oxidant or the presence of an oxidizing directing group.[7] We developed the idea of using TMS-acetylene as a precursor for the direct vinylation of secondary benzamides under redox

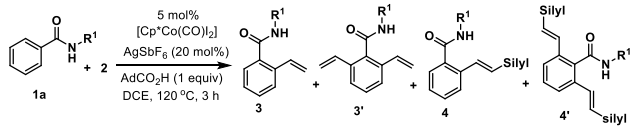
neutral conditions. To our delight, under the reaction conditions, the reaction of TMS acetylene with benzamide afforded the corresponding styrene derivative (Scheme 1b). Interestingly, the -NH group of the amide remains intact under the reaction conditions and the possible cyclic products were not observed in the reaction (Scheme 1c).

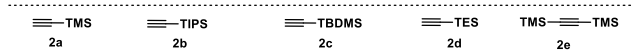
Further, we examined the scope of the reaction employing (arylalkynyl)silanes, which are found to be better precursors than the terminal alkynes for obtaining the corresponding disubstituted alkenes. Moreover, desilylation of (arylalkynyl)silanes is one of the easiest ways to obtain terminal alkynes.[8] Thus, in continuation of our efforts,[9] herein we report an air-stable, abundant, and cost effective[10] Co(III)-catalyst for the desilylative direct *ortho*-vinylation of secondary benzamides, in which the counter anion, SbF_6^- plays a crucial role in the desilylation.

Results and Discussion

Optimization of the reaction started by examining the reaction of *N*-methyl benzamide **1a** (0.3 mmol) with TMS acetylene **2a** (0.36 mmol). The reaction in the presence of $Cp^*Co(CO)I_2$ (5 mol%) as a catalyst, $AgSbF_6$ (20 mol%) as an activator and $AdCO_2H$ (1 equiv) as an additive in DCE (2 mL) at 120 °C for 3 h furnished the corresponding alkenylated product **3** in 48% yield along with the dialkenylated product **3'** in 5% yield (entry 1, Table 1, and also see SI, Table SI-1). Further investigation of various solvents, activators, and additives (see SI, Table S-1, S-2, and S-3) revealed that the reaction proceeds well in DCE (2 mL) as a solvent in the presence of $AgSbF_6$ (20 mol%) and $AdCO_2H$ (1 equiv). During the optimization studies, the reaction of **1a** with various silyl acetylenes such as (triisopropylsilyl)acetylene (**2b**), (*tert*-butyldimethylsilyl)acetylene (**2c**), (triethylsilyl)acetylene (**2d**), and bis-(trimethylsilyl) acetylene (**2e**) was examined. The reaction of **1a** with **2b** did not furnish the product **3** (entry 2, Table 1). The reaction of **1a** with **2c** furnished the product **3** in 55% yield along with divinylated product **3'** in 8% (entry 3). The reaction of **1a** with **2d** and **2e** furnished the product **3** in 20 and 40% yields, respectively (entries 4 and 5). Replacing the methyl group of amide **1a** with isopropyl or phenyl group did not bring any significant change in the yield of the reaction (entries 6 and 7). Performing the reaction **1a** with **2c** at 60 °C furnished the product **3** in a trace amount, and the corresponding mono- and di-activated vinylsilanes **4ac** and **4ac'** were obtained in 54, and 8% yields, respectively (entry 8 and see SI, Table S-5). Efforts to improve the yields of vinylated product **3** or/and vinylsilane **4** by varying reaction conditions were unsuccessful (see the SI for more details).

Table 1. Optimization studies[a]



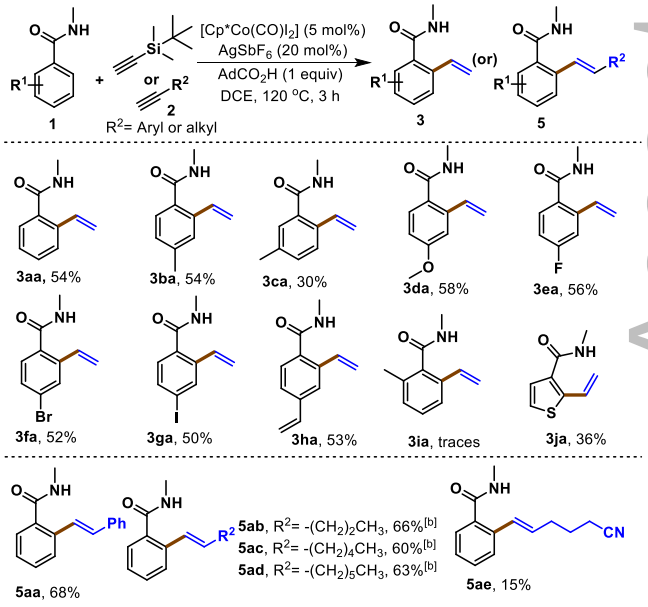


entry	R^1	2	NMR yield (%) [b] 3	3'	4	4'
1	Me	2a	50	5	nd	nd
2	Me	2b	nd	nd	nd	nd
3	**Me**	**2c**	**55**	**8**	**nd**	**nd**
4	Me	2d	20	traces	nd	nd
5	Me	2e	40	4	nd	nd
6	*i*Pr	2c	22	traces	nd	nd
7	Ph	2c	30	traces	nd	nd
8[c]	Me	2c	traces	nd	54	8

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol), $[Cp^*Co(CO)I_2]$ (5 mol%), $AgSbF_6$ (20 mol%), $AdCO_2H$ (1 equiv), DCE (2 mL), at 120 °C for 3 h. [b] Measured by ^1H NMR with terephthalaldehyde as an internal standard. [c] At 60 °C for 12 h. nd=not detected

Using the optimal conditions (entry 3, Table 1), the scope of the reaction with benzamide derivatives has been examined (Scheme 2). Thus, 4-Me, 3-Me, and 4-OMe substituted *N*-methyl benzamides afforded the corresponding vinylated products **3ba**, **3ca**, and **3da** in 54, 30 and 58% yields, respectively. In the case of 3-methyl-substituted benzamide, we observed the vinylation at the sterically free *ortho* position, and the other regioisomer was not observed. It is worth noting that the other uncommon regioisomer was observed by Hamilton and Whiteoak in their reaction of 3-fluorobenzamide with methyl vinyl ketone.[11] Halogenated *N*-methylbenzamides underwent smooth

Scheme 2. Substrate scope for vinylation of amides[a]



[a] Under standard conditions. [b] 2 equiv of **1** and 1 equiv of **2** was used.

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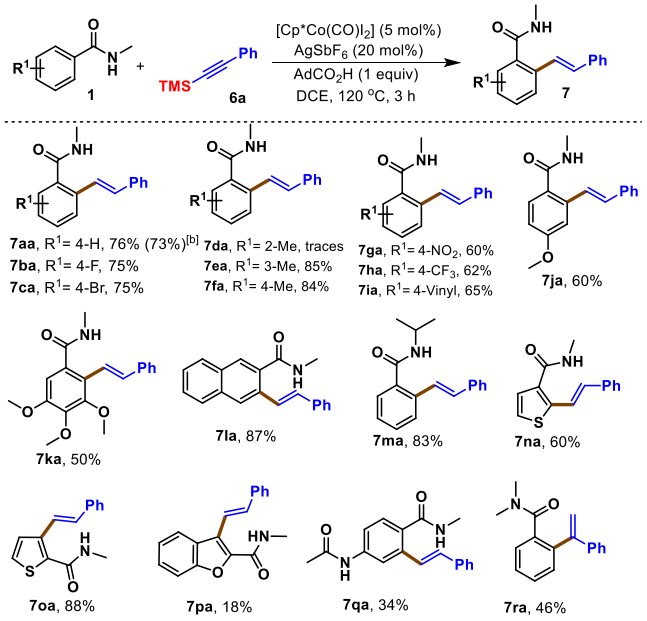
reaction furnishing the products **3ea**, **3fa**, and **3ga** in moderate yields (56, 52, and 50% yields, respectively). The reaction of *N*-methyl-4-vinyl benzamide with **2a** furnished the product **3ha** in 53% yield. Substituting methyl group at the *ortho*-position of **1a** furnished the product **3ia** in a trace amount, which might be due to the steric factor. Thiophene derived amide, a heterocyclic amide, afforded the product **3ja** in 36% yield. Additionally, we have examined the reaction of terminal alkynes such as phenylacetylene, 1-pentyne, 1-heptyne, 1-octyne, and 5-cyano-1-pentyne with **1a** under a slightly modified reaction conditions, which delivered the corresponding alkenylated products **5aa**, **5ab**, **5ac**, **5ad**, and **5ae** in 68, 66, 60, 63, and 15% yields, respectively (Scheme 2). However, in all the cases, the unreacted *N*-methyl benzamide was recovered.

As most of the phenylacetylene derivatives are obtained from the desilylation of (arylalkynyl)silanes,[8] we have turned our attention to explore the scope of the reaction of amide **1a** with (phenylalkynyl)silane **6a** (Scheme 3). Thus, the reaction of 1-phenyl-2-trimethylsilylacetylene **6a** with the amide **1a** under optimal conditions (Table 1, entry 3) furnished the corresponding alkenylated product **7aa** in 76% isolated yield along with the diactivated product **7aa'** in 13% yield (see SI, Table S-6). The reaction of **6a** with benzamide having methyl and halogen substitution at *meta*- and *para*-position provided the corresponding alkenylated products **7aa-7fa** in good to excellent yields, whereas a methyl substitution at the *ortho*-position of **1a** under optimal conditions afforded the product **7da** in a trace amount. Benzamide derivatives having substitution with electron-withdrawing groups such as NO_2 and CF_3 at the *para*-position underwent smooth reactions and gave the desired products **7ga** and **7ha** in good yields.

Scheme 3. Scope of alkenylation of secondary benzamide derivatives[a]

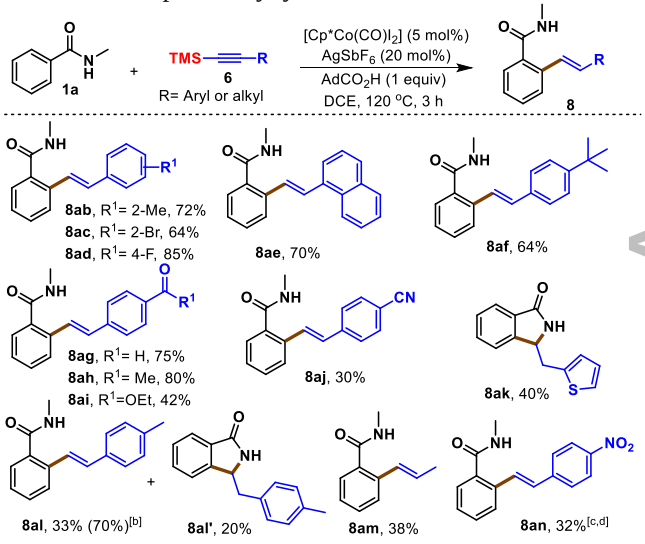


[a] Under standard conditions. [b] 3 mmol scale.

Benzamides substituted with vinyl, and an electron-donating methoxy group at the *para*-position also reacted with **6a** affording the products **7ia-7ka** in moderate yields. 2-Napthamide and isopropyl protected benzamide furnished the products **7la** and **7ma** in 87 and 83% yields, respectively. Additionally, heterocyclic amides such as thiophene and benzofuran derived amides displayed a good reactivity with the acetylene **6a** to furnish the products **7na-7pa** in 60, 88, and 18% yields, respectively. 4-Acetamido-*N*-methylbenzamide reacted with **6a**, selectively at the *ortho*-position of the amide and furnished the corresponding product **7qa** in 34% yield. Interestingly, subjecting the tertiary benzamide such as *N*,*N*-dimethybenzamide under the optimal conditions, furnished the *exo*-alkenylated product **7ra** in 46% yield which may be due to the steric crowding on nitrogen. A scale-up experiment has been performed in 3 mmol scale to showcase the efficacy of the reaction, which afforded the product **7aa** in 73% yield.

The scope of the reaction was further extended by reacting (arylalkynyl)silane derivatives with *N*-methyl benzamide **1a** (Scheme 4). Thus, the reaction of **1a** with (arylalkynyl)silanes possessing alkyl/halogen substitution on the aromatic ring proceeded well under the optimal conditions furnishing the products **8ab-8af** in good to excellent yields. (Arylalkynyl)silanes that contained synthetically useful functional groups such as aldehyde, ketone, ester, and cyano groups are also well tolerated and afforded the products **8ag-8aj** in good to moderate yields. However, the thiophene-derived alkynylsilane furnished the corresponding cyclic product **8ak** in 40% yield which might be due to the presence of an electron-rich heteroaryl ring that can lead to an acid promoted cyclization. Reaction of (arylalkynyl)silane (**6l**) with 4-methyl substitution on

Scheme 4. Scope of alkynylsilane derivatives[a]



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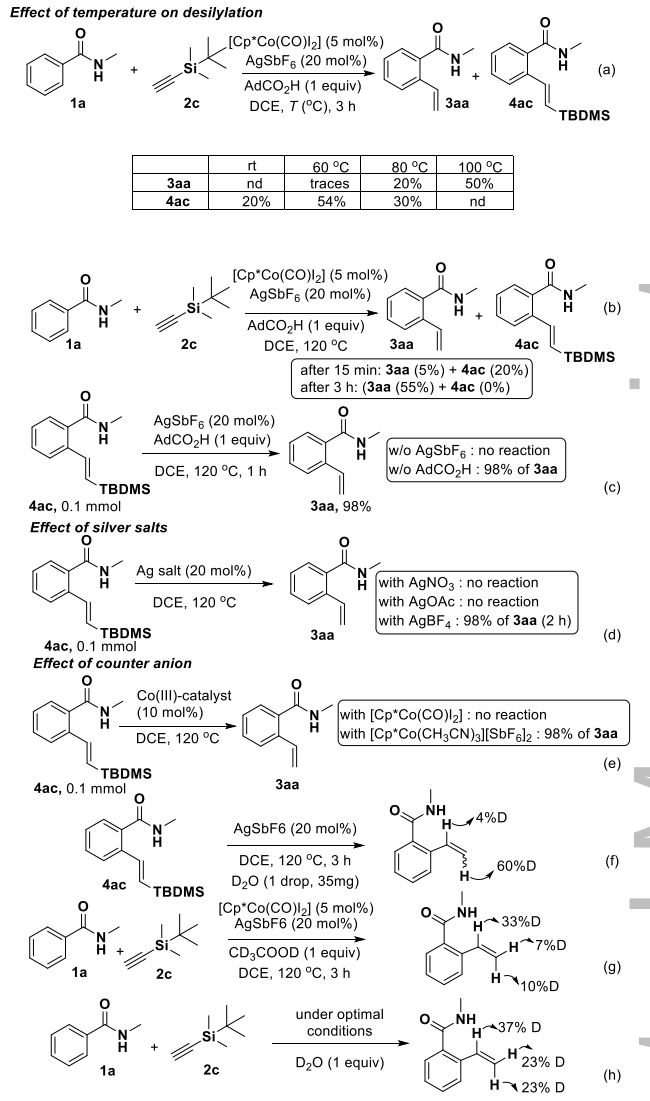
[a] Under standard conditions. [b] 2 equiv of **1a**, 1 equiv of **6** and 20 mol% of $AdCO_2H$ was used. [c] NMR yield. [d] Inseparable mixture along with **1a**.

the aromatic ring with **1a** furnished the corresponding alkenylated product **8al** along with the cyclic product **8al'** in 33 and 40% yield, respectively. However, the yield of **8al** was improved to 70% by using 2 equiv of **1a** and 20 mol% of $AdCO_2H$ (Scheme 4). This may be due to the reduced amount of acid additive present in the reaction medium. The reaction of an alkyl group substituted alkynylsilane also furnished the corresponding alkenylated product **8am** in 38%. (arylalkynyl)silane that contained electron-withdrawing group such as a nitro group on aryl ring furnished the product **8an** in 32% yield (^{1}H NMR yield) as an inseparable mixture along with **1a**.

To probe the reaction mechanism, a few control experiments were carried out. Variation of the temperature indicated that the desilylation requires a high temperature (Scheme 5a). The reaction at 80 °C furnished 20% of **3aa** and 30% of **4ac** indicating that **4ac** can be the intermediate in the reaction (Scheme 5a). Further, when the reaction was performed for only 15 min under optimal conditions, the products **3aa** and **4ac** were obtained in 5 and 20% yields, respectively (Scheme 5b). This reaction emphasizes that **4ac** is the probable intermediate. To find the reagent that is responsible for the desilylation, a reaction of **4ac** with $AgSbF_6$ and $AdCO_2H$ was performed, which furnished **3aa** in 98% yield. Surprisingly, the same reaction furnished the product **3aa** even in the absence of $AdCO_2H$ without affecting the yield of **3aa** (Scheme 5c). This experiment clarifies that there is no role of the acid in the desilylation. Further screening of different silver salts has been carried out (Scheme 5d). Thus, the reaction of **4ac** with $AgNO_3$ or AgOAc did not furnish the corresponding desilylated product **3aa**, whereas the similar reaction of **4ac** with $AgBF_4$ furnished the corresponding desilylated product **3aa** in 98% yield. These experiments revealed that fluoride source is necessary for the desilylation. This observation was further confirmed by the reaction of **4ac** with $Cp^*Co(CO)I_2$, which did not furnish the product **3aa**, while the reaction of **4ac** with $[Cp^*Co(CH_3CN)_3][SbF_6]_2$ furnished the product **3aa** in 98% yield (Scheme 5e). From these experiments, we conclude that the counter anion plays a crucial role in the desilylation of **4ac**. The desilylation was also observed even in the absence of $AdCO_2H$ (Scheme 5c), indicating that the protodesilylation is occurring with the help of moisture present in the medium. To ensure this observation, **4ac** was reacted with $AgSbF_6$ in the presence of D_2O (1 drop), which led to the deuteration at the terminal carbon (60%) confirming our assumption (Scheme 5f). Treating **1a** with **2c** under the optimal conditions with CD_3COOD, instead of $AdCO_2H$, resulted in the formation of the product with 33% of deuteration at the α-position of the olefinic carbon and, 7 and 10% of terminal carbon of the olefin (Scheme 5g). This reaction suggests the

Scheme 5. Control experiments



involvement of $AdCO_2H$ in the protodemetallation. Performing the same experiment in the presence of D_2O (1 equiv) under the optimal conditions furnished the product with 23% deuteration at the terminal carbon, which further confirmed the involvement of moisture during desilyation step (Scheme 5h).

Based on the control experiments, previous studies,[4f] and literature precedence,[9,11] a plausible mechanism has been proposed (Scheme 6). The *in situ* generated catalytically active species **A** reacts with **1a** leading to the cobaltacycle **B**. Further insertion of alkyne **2c** to **B** forms the intermediate **C**. Subsequently, $AdCO_2H$ promotes the protodemetallation of **C** forming the corresponding vinylsilane **4ac** and regenerating the active catalyst **A**. Finally, **4ac** undergoes desilylation in the presence of the counter anion SbF_6^-, which is present in the medium, furnishing the product **3aa**.

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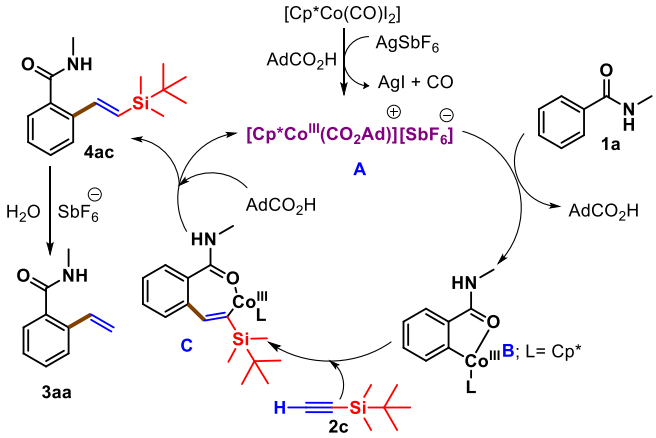
Scheme 6. Plausible Mechanism



Conclusion

In conclusion, we have developed a Co(III)-catalyzed desilylative direct *ortho*-vinylation of N-methyl benzamide derivatives using alkynyllsilane as a coupling partner. The salient feature of the reaction is the exclusive formation of the alkenylated product rather than the cyclic products. The alkynylsilane was found to be an excellent alternative for terminal alkynes. The mechanistic studies revealed that the counter anion, SbF_6^-, is playing a crucial role in desilylation, which is a novel and unprecedented observation.

Experimental Section

General information

All reactions were carried out using distilled solvents. Reactions were monitored by using precoated silica TLC plates. Mass spectra were recorded on EI, and ESI (TOF) modes. NMR spectra were recorded in at 400 MHz spectrometers in $CDCl_3$, DMSO-d_6, tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal reference for ^1H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$; δ = 77.00 ppm and DMSO-d_6; δ = 39.52 ppm) was used as internal standard for ^{13}C NMR. Column chromatography was carried out on silica gel 230-400 mesh or 100-200 mesh (Merck), and thin-layer chromatography was carried out using SILICA GEL GF-254. Chemicals obtained from commercial suppliers were used without further purification.

Experimental procedure for *ortho* alkenylation of benzamide derivatives (3aa-3ja, 7aa-7ra and 8ab-8an)

In a 8-mL screw-cap reaction vial, *N*-methyl benzamide derivative (0.3 mmol), (tert-butyldimethylsilyl)acetylene or 1-phenyl-2-trimethylsilylacetylene derivatives (0.36 mmol), cobalt catalyst (Cp*$CoCOI_2$, 7.1 mg, 5 mol%), AdCOOH (54 mg, 1 equiv), $AgSbF_6$ (20.6 mg, 20 mol%) in DCE (2 mL) were taken. The vial was sealed with a screw cap and placed in a pre-heated metal block at 120 °C, and the reaction mixture was stirred at the same temperature for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/petroleum ether mixture.

Note: Compounds **7ma** and **8ai** were purified by using EtOAc/DCM mixture instead of EtOAc/petroleum ether mixture.

Experimental procedure for synthesizing vinylsilane (4ac)

In a 8-mL screw-cap reaction vial, *N*-methyl benzamide derivative (40.5 mg, 0.3 mmol), (tert-butyldimethylsilyl)acetylene (50.4 mg, 0.36 mmol), cobalt catalyst (Cp*$CoCOI_2$, 7.1 mg, 5 mol%), AdCOOH (54 mg, 1 equiv), $AgSbF_6$ (20.6 mg, 20 mol%) in DCE (2 mL) were taken. The vial was sealed with a screw cap and placed in a pre-heated metal block at 60 °C, and the reaction mixture was stirred at the same temperature for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and concentrated under vacuum. The crude products were purified on a silica gel column using EtOAc/petroleum ether mixture.

Acknowledgments

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