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# Regioselective Synthesis of 2-Vinylanilines Using *O*-aroyloxycarbamates by Sequential Decarboxylation/Amination/Heck Reaction

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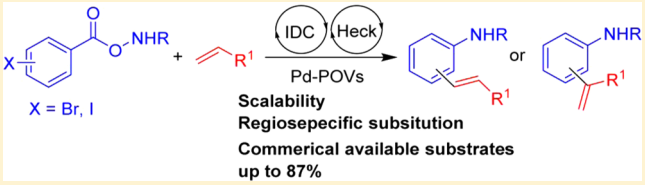
Supporting Information

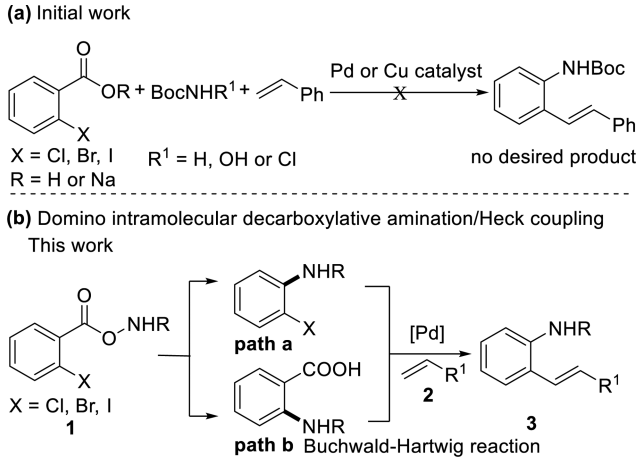
**ABSTRACT:** A new sequential approach for 2-vinylanilines utilizing aryl carboxylic acids as stable, inexpensive and widely available arylating reagents is described. Employing a Pd-POVs catalyst system, this protocol is not only overcoming the restriction barrier of decarboxylative coupling to *ortho*-substituted substrates, but also provides site-special to create new C($sp^2$)-N and C($sp^2$)-C($sp^2$) bonds. Mechanistic experiments suggest the cleavage of C($sp^2$)-COOH gives priority to C($sp^2$)-X bond in this reaction.




Sequential reactions are a powerful method for the formation of two or more bonds under identical reaction conditions without isolating the intermediates or adding reagents.[1] The well-known Heck coupling reactions are some of the most direct methods to form carbon−carbon bond in organic synthesis.[2] A diverse array of sequential reactions employing the Heck coupling have been established, such as Heck−C-H activation,[3] Heck-cyanation,[4] Heck-carbohalogenation,[5] and Heck-aza-Michael[6] et al. This important and classic transition-metal catalyzed Heck-type reaction has been reported variously. However, to the best of our knowledge, no report has appeared using intramolecular decarboxylative amination and Heck coupling for the synthesis of 2-vinylanilines.

2-Vinylaniline derivatives are widely used intermediates in organic chemistry for the synthesis of biologically related heterocyclic compounds.[7] Due to 2-vinylaniline usefulness, many elegant methods have been developed for the synthesis of 2-vinylanilines, including Suzuki,[8] Stille,[9] Mizoroki-Heck couplings,[10] C−H activation,[7c] and reduction.[11] Despite this progress, multiple and harsh reaction conditions of these methods are challenging, the high cost and the low stability of 2-substituted anilines are still deficient.[12] Consequently, a more general strategy from easily available starting materials is still demanded. Herein we wish to report a novel sequential approach for the synthesis of 2-vinylanilines utilizing aryl carboxylic acids as stable, inexpensive, and widely available arylating reagents. In this new method, there are two possible pathways. Path a, the intramolecular decarboxylative coupling (IDC) reaction, which has been reported in our research group.[13] Path b, the Buchwald-Hartwig reaction, which has been reported as an elegant method to construct C−N bond (Scheme 1b, path b).[14] Ignore the differences of both cases, the same product **3** was obtained. Due to the C($sp^2$)-COOH bond being more difficult to cleave than C($sp^2$)-X bond according to the Buchwald-Hartwig reaction.[15] It is natural to expect that the new method should enable the path b. We initially attempted a

**Scheme 1. Synthesis of 2-Vinylanilines**




metal-catalyzed sequential reaction between alkyl hydroxycarbamates and carboxylic acid or carboxylates with styrene, unfortunately, these reactions did not deliver the desired products (Scheme 1a).

To realize the decarboxylative amination of aroyloxycarbamates from inert aromatic acid derivatives, the IDC reaction was designed and the condition needs to be efficiently optimized. Fortunately, we found **A** (Figure 1) is an excellent catalyst using the sequential decarboxylation/amination/Heck reaction for the synthesis of 2-vinylanilines. Based on its remarkable activity in acidic and oxidation catalysis with wide structural diversity and O-enriched surfaces by our previous work, we decided to use the Pd-POVs catalyst and exploit the potential application of Pd-POVs in the sequential reaction. Polyoxometalates (POMs) have exhibited excellent perform-

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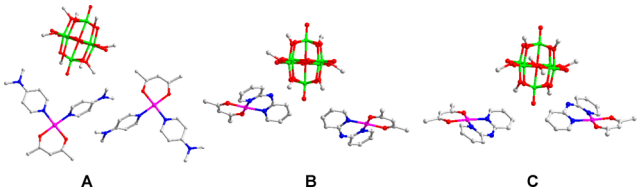
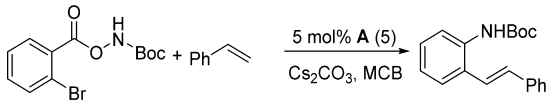



**Figure 1.** Crystal structure of $[Pd(DMAP)_2(acac)]_2[V_6O_{11}(O\text{-}Me)_8]\cdot H_2O$ (**A**), $[Pd(dpa)(acac)]_2[V_6O_{13}(OMe)_6]$ (**B**), $[Pd(dpa)(acac)]_2[V_6O_{11}(OMe)_8]$ (**C**). Color code: Pd, pink; V, green; N, blue; O, red; C, gray.

ance as a class of nanosized metal-oxo clusters in both acidic and oxidation catalysis.[16] Notably various POMs-catalyzed pathways have been reported with excellent catalytic activity.[17] The Lindqvist $[V_6O_{19}]^{8-}$ anion is one of the classical POM structures. The substitution of bridging oxygen atoms in the Lindqvist $[V_6O_{19}]^{8-}$ with oxygen donor-ligands is proven to be another effective method to compensate the negative charge and stabilize the cluster.[18] However, it is worth mentioning that alkoxohexavanadates have fascinating electronic, magnetic, photochemical properties and potential catalytic application.[19] Until now, very few examples about their catalytic property have been reported.[20] Due to alkoxohexavanadates being extremely susceptible by trace amount of water. Therefore, our previous work displayed the synthetic methods for stable and highly active catalysts based on alkoxohexavanadates.[21] The Pd-complex was selected as countercation to couple with alkoxohexavanadate cluster through electrostatic interaction. Pd-POVs (**A**, **B**, **C**) (Figure 1) were synthesized in a simple and straightforward method. The above catalysts are stable in the air and aqueous solution, showing unexpected catalytic activities in the oxidation of benzyl-alkanes. To exploit the property of this kind of catalyst, we found **A** is an excellent catalyst using the sequential decarboxylation/amination/Heck reaction for the synthesis of 2-vinylanilines. Moreover, no report has appeared for this sequential reaction.

To further screen the decarboxylative amination/Heck couping condition of 2-halogen-aroyloxycarbamates from inert aromatic acid derivatives with olefin, the activity of the Pd-POVs catalyst was tested for the sequential reaction of IDC and Heck coupling for the synthesis of 2-vinylanilines from *tert*-butyl ((2-bromobenzoyl)oxy)carbamate with styrene as the model substrate. As shown in Table 1, the reaction occurred smoothly in the presence of **A**, affording *tert*-butyl-(2-styrylphenyl)carbamate (**3a**) in 80% yield (Table 1, entry 5). According to the results of the catalysts screening, **A** is the best catalyst for this reaction in terms of the product selectivities. In the absence of the catalyst or base no product **3a** was observed (Table 1, entries 1−3). To probe the role of Pd-complex in the IDC reaction, $PdCl_2$/DMAP/Hacac (1:2:1) were used as catalyst system in 43% yield at 100 °C in chlorobenzene (Table 1, entry 4). Other Pd-POVs were also investigated in the reaction including **B** and **C** to afford the corresponding product **3a** in 7% and 11%, respectively (Table 1, entries 8−9). Considering the influence of temperature on decarboxylative reaction, different temperature were also investigation in this IDC reaction. From the above results, the *tert*-butyl carbamate (Boc) group was deprotected at 120 °C with 1.0 equiv $Cs_2CO_3$ in chlorobenzene yield 73% (Table 1, entry 10). We were pleased to see that the 1 equiv $Cs_2CO_3$ performed best to the **3a** (Table 1, entries 5, 11−12). Increasing the amount of catalyst did not improve the yield (Table 1, entry 15). The

**Table 1. Optimization for the Reaction Conditions**[a]




1 2 3

| entry | catalyst | base (equiv) | *T* (°C) | yield (%)[b] |
|---|---|---|---|---|
| 1 | | | 100 | 0 |
| 2 | | $Cs_2CO_3$ | 100 | 0 |
| 3 | **A** | | 100 | 0 |
| 4 | $PdCl_2$/DMAP/Hacac | $Cs_2CO_3$ | 100 | 43 |
| 5 | **A** | $Cs_2CO_3$ | 100 | 80(79)[c] |
| 6 | **B** | $Cs_2CO_3$ | 100 | 7 |
| 7 | **C** | $Cs_2CO_3$ | 100 | 11 |
| 8 | **A** | $Cs_2CO_3$ | 90 | 71 |
| 9 | **A** | $Cs_2CO_3$ | 110 | 77 |
| 10 | **A** | $Cs_2CO_3$ | 120 | 73 |
| 11 | **A** | $Cs_2CO_3$ (0.5) | 100 | 48 |
| 12 | **A** | $Cs_2CO_3$ (1.5) | 100 | 26 |
| 13 | **A** (1.0 mol%) | $Cs_2CO_3$ | 100 | 52 |
| 14 | **A** (2.5 mol%) | $Cs_2CO_3$ | 100 | 66 |
| 15 | **A** (7.5 mol%) | $Cs_2CO_3$ | 100 | 80 |
| 16 | **A** | $Cs_2CO_3$ | 100 | 80[d] |
| 17 | $PdCl_2(PPh_3)_2$ | $Cs_2CO_3$ | 100 | 75 |

[a]Reaction conditions: **1** (0.20 mmol), **2** (0.24 mmol), catalyst (5.0 mol%), base (0.20 mmol, 1.0 equiv) in chlorobenzene (MCB) (2 mL) at 100 °C for 10 h. [b]Yields determined by GC analysis using biphenyl as internal standard. [c]Isolated yield. [d]10 mmol scale.

reactions were also successfully performed at large scales without significant loss of yield (entry 16). Thus, the optimized reaction conditions are as follow: 5 mol% **A** and 1 equiv of $Cs_2CO_3$ in 2.0 mL of MCB at 100 °C for 10 h.

With the optimized reaction conditions in hand, we examined the scope of the sequential reaction (Table 2). The substrate scope of alkenes were investigated by the reaction of 2-halogen-aroyloxycarbamates with various substituted alkenes. Surprisingly, different substituted phenyl ring alkenes gave the corresponding products **3** in good yields with slight influence. It is shown that electron-withdrawing is better than electron-donating substituted phenyl ring alkenes for the sequential reaction (Table 2, entries 2, 3, 6, 7, 8, 11). The influence of *ortho*-, *meta*-, *para*-substitutions of phenyl ring alkenes were also tested, and with the *para*-, *meta*-, *ortho*- sequence the yield gradually decreases (Table 2, entries 7, 9, 10). The substituted alkyl olefins were also investigated in this optimized conditions. Thus, the allyl phenyl ether **2h** was reacted with **1c** to furnish **3h** in 78% yield (Table 2, entry 12). The methyl acrylate **2i** was reacted with **1c** to obtain **3i** in 55% yield (Table 2, entry 13). It is worth noting that the alkenyl ether compound gave the chemoselectivity products, such as ethoxyethene **2j**, 2-methyl-1-(vinyloxy)propane **2k**, 1-(vinyloxy)butane **2l** reacted with **1c** to afford *tert*-butyl (2-(1-ethoxyvinyl)phenyl)carbamate **3j**, *tert*-butyl (2-(1-isobutoxyvinyl)-phenyl)carbamate **3k** and *tert*-butyl (2-(1-butoxyvinyl)phenyl)- carbamate **3l** in 62, 80, and 86% yields, respectively (Table 2, entries 14−16).[2f,g] Furthermore, 2-halogen-aroyloxycarbamates, such as 2-bromo- (**1a**), 2-chloro- (**1b**), and 2-iodine- (**1c**), substituted substrates were investigated in the reaction. Fortunately, the 2-bromo-substituted substrates (**1a**) reacted with different substitutions of phenyl ring alkenes **2a**, **2b**, **2c** to give the **3a**, **3b**, **3c** with good yields. The reaction time increased up to 10 h comparing



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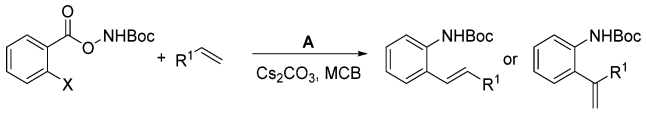
**Table 2. Substrate Scope**[a]




1 2 3a-3i 3j-3l

| entry | X | $R^1$ | product (time) | yield (%)[b] |
|---|---|---|---|---|
| 1 | Br (**1a**) | $C_6H_5$ | **3a** (10 h) | 79 |
| 2 | Br | 4-$MeC_6H_4$ | **3b** (10 h) | 81 |
| 3 | Br | 4-$ClC_6H_4$ | **3c** (10 h) | 87 |
| 4 | Cl (**1b**) | $C_6H_5$ | **3a** (10 h) | trace |
| 5 | I (**1c**) | $C_6H_5$ | **3a** (8 h) | 78 |
| 6 | I | 4-$MeC_6H_4$ | **3b** (8 h) | 80 |
| 7 | I | 4-$ClC_6H_4$ | **3c** (8 h) | 86 |
| 8 | I | 4-$FC_6H_4$ | **3d** (8 h) | 85 |
| 9 | I | 2-$ClC_6H_4$ | **3e** (8 h) | 74 |
| 10 | I | 3-$ClC_6H_4$ | **3f** (8 h) | 82 |
| 11 | I | 4-$MeOC_6H_4$ | **3g** (8 h) | 76 |
| 12 | I | $C_6H_5OCH_2$ | **3h** (14 h) | 78 |
| 13 | I | COOMe | **3i** (10) | 55 |
| 14 | I | *n*-EtO | **3j** (6 h) | 62 |
| 15 | I | *i*-BuO | **3k** (6 h) | 80 |
| 16 | I | *n*-BuO | **3l** (6 h) | 86 |

[a]Reaction conditions: **1** (0.50 mmol), **2** (0.6 mmol), **A** (5 mol%), $Cs_2CO_3$ (0.50 mmol) in chlorobenzene (MCB) (5 mL) at 100 °C. [b]Yield of isolated product. And there is trace of (*Z*)-style product be detect by TLC (**3a**−**3i**) (*E*/*Z* > 99/1). The regioselectivity of entries 14−16 was detected by crude H NMR about 11/89. The 11 is linear Heck product (*E*/*Z* = 51/49).

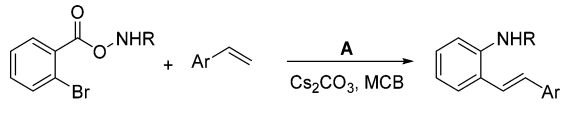
with **1c** (Table 2, entries 1−3). Unfortunately, trace of product **3a** was detected, when 2-chloro- (**1b**) substituted substrates reacted with styrene **2a** (Table 2, entry 4). As described above, the reactive activity of the halogeno-substrates can be found in the following order: 2-I, 2-Br, and 2-Cl.

In addition to the scope of aroyloxycarbamates, we also briefly investigated the feasibility of halogen-aroyloxycarbamates with various valuable carbamates as additional types of deprotectable amination sources. We were pleased to see that a wide range of carbamates were readily employed with the present Pd-POVs catalyst system under optimized condition (Table 3). In this approach, benzyloxycarbonl (Cbz) could be tolerated at the optimized condition (**3aa**). In addition, various substituted carbamates were employed, including methyl, ethyl, isopropyl, isobutyl, *n*-butyl, *n*-pentyl, and even *n*-hexyl groups, with satisfactory yields (**3ab**−**3ah**). The *meta*-, *para*-bromo substitutions of phenyl ring of aroyloxycarbamates were also examined. The *meta*-bromo substitutions could be transformed into corresponding products in good yields (**3ai**−**3ak**). But the reaction is complex and trace desired product **3al** when *para*-bromo substitutions aroyloxycarbamates reacted with styrene.

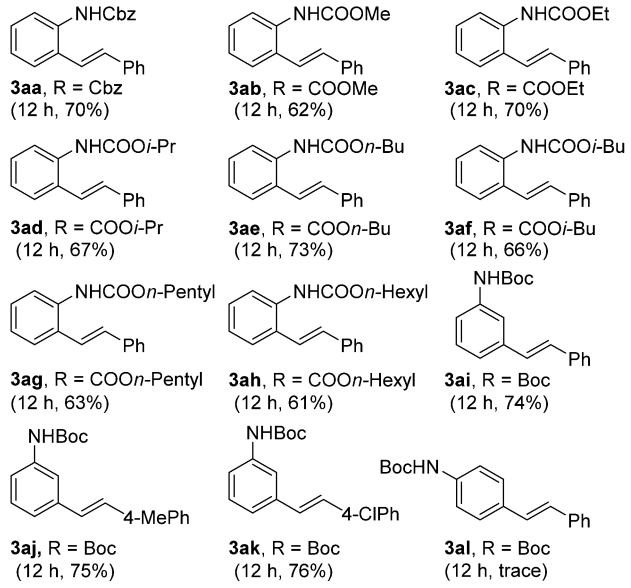
The synthetic utility of the 2-vinylanilines was exhibited by their further transformation to 2-substituted indole (Scheme 2). It was demonstrated that 2-vinylanilines **3a**, in the presence of *N*-Iodosuccinimide (NIS) under the mild condition to synthesis the 2-phenyl indole in moderate yields **4a**.[22] And **3a** could translate into *tert*-butyl (Z)-(2-styrylphenyl)carbamate **5a** smoothly using the high pressure mercury lamp as the light resource. It has been reported the conversion of *cis*-Stilbene to *trans*-Stilbene using organolithium reagent by O'Shea's group.[23]

Based on previous work[7,12] and our mechanistic experiments, a plausible catalytic cycle of this sequential approach is proposed (Scheme 3). Interestingly, when the sequential

**Table 3. Substrate Scope**[a]

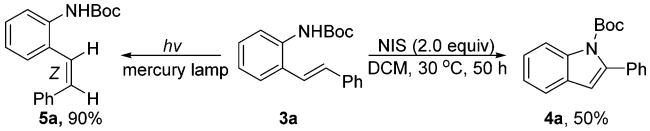



1 2 3

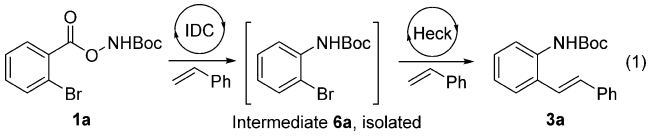



[a]Reaction conditions: **1** (0.50 mmol), **2** (0.6 mmol), **A** (5 mol%), $Cs_2CO_3$ (0.50 mmol) in chlorobenzene (MCB) (5 mL) at 100 °C. [b]Yield of isolated product. And there are trace of (*Z*)-style product be detect by TLC (*E*/*Z* > 99/1).

**Scheme 2. Utility of the 2-Vinylanilines**




**Scheme 3. Proposed Sequential Reaction Catalytic Cycle**




reaction was carried out, the regioselectively intermediate of **6a** was observed, suggesting that the mechanistic of this sequential reaction is the path a (Scheme 1a), we were confirmed by recent reports from Glorius.[24] Then we proposed sequential reaction catalytic cycle is IDC[13] and Heck coupling.[25] In addition, the intramolecular decarboxylative amination is faster than the Heck reaction from the monitored of the sequential approach.

To verify whether the catalysis is truly homogeneous or not, the model reaction of *tert*-butyl ((2-bromobenzoyl)oxy)-carbamate with styrene was carried out under the optimized conditions, and the reaction was filtered by filter paper from the reaction mixture at 40% formation of **3a**. After filtration, the reaction was added one equivalent of base and stirred for another 3 h. It is still converted to **3a** in 80% yield. In addition, the filtered solids were washed with chlorobenzene, air-dired,



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and then reused directly in a model reaction without further purification. The results showed that no product **3a** was obtained. Therefore, the catalysis is truly homogeneous. In this vein, five cycles were carried without loss of reactivity on the model reaction (Figure 2), showing that the catalyst is easily recovered without its removal from the solvent.

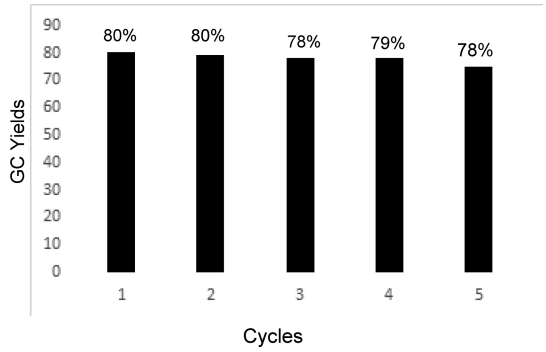


**Figure 2.** Reusability of catalyst.

In conclusion, we have developed a new approach for the regioselective synthesis of 2-vinylanilines using Pd-POVs catalyst system from aryl carboxylic acids. The route is the first example for 2-vinylanilines through sequential approach by sequential decarboxylation/amination/Heck reaction from aroyloxycarbamates and alkenes. Using an in situ generated aroyloxycarbamates from inexpensive aromatic acid with carbamates, various substituted vinylanilines were site-selectively synthesized. Given the excellent functional group compatibility and the ubiquity of amine functional groups, the Pd-POVs catalyst system will streamline the synthesis of vinylanilines. This method opens many opportunities for regioselective C−N bonds construction using carboxylic acids by creating alternatives to conventional synthetic routes.

## EXPERIMENTAL SECTION

**General Remarks.** All commercially available reagents were used without further purification. Unless stated otherwise, all reactions were carried out in Schlenk tube under a dry argon or nitrogen atmosphere. All solvents were purified and dried according to standard methods prior to use. Column chromatography was performed on silica gel (200−400 mesh). GC-MS data were performed on Agilent 7890A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (HP-5 30 m × 0.25 $\mu$m) using a flame ionization detector. Melting points were determined using an X-4 apparatus and are uncorrected. The FTIR spectra were recorded from KBr pellets in the range 4000−400 $cm^{-1}$ on Nicolet 170 SXFT/IR spectrometer. NMR spectra were taken with a Bruker 400 spectrometer at 400 MHz ($^1H$) and 101 MHz ($^{13}C$) using $CDCl_3$ as the solvent with TMS as internal standard. Chemical shifts were reported in ppm referenced to the center of a triplet at 77.0 ppm of chloroform-*d*. HRMS was performed on TOF LC-MS in ESI mode.

**Synthesis of $[Pd(DMAP)_2(acac)]_2[V_6O_{11}(OMe)_8]\cdot H_2O$ (A).** $VO(acac)_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.8 mmol) were added to 6 mL of methanol. The resulting solution was stirred at room temperature for 20 min, and then DMAP 2,2′-dipyridine amine (48.0 mg, 0.4 mmol) and $Pd(OAc)_2$ (44.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 65.6%.[21]

**Synthesis of $[Pd(dpa)(acac)]_2[V_6O1_3(OMe)_6]$ (B).** $VO(acac)_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.6 mmol) were added to 6 mL of methanol. The resulting solution was stirred at room temperature for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol) and $Pd(OAc)_2$ (44.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 64.3%.[21]

**Synthesis of $[Pd(dpa)(acac)]_2[V_6O_{11}(OMe)_8]$ (C).** $VO(acac)_2$ (0.6 mmol, 159.1 mg) and triethylamine (0.8 mmol) were added to 6 mL of methanol. The resulting solution was stirred at room temperature for 20 min, and then 2,2′-dipyridine amine (34.3 mg, 0.2 mmol) and $Pd(OAc)_2$ (44.9 mg, 0.2 mmol) were successively added. The reaction mixture was stirred for 12 h. From the resulting solution, yellow crystals suitable for X-ray diffraction grew after leaving the solution to stand for a week. Yield: 62.5%.[21]

**Representative Procedure for the Synthesis of *O*-Aroyloxycarbamates.** *General Procedure for the Preparation of N-Hydroxyl Carbamate (BocNHOH).* *N*-hydroxyl *tert*-butyl carbamate was prepared from hydroxylamine hydrochloride with $(Boc)_2O$, according to a known procedure. A suspension of $NH_2OH\cdot HCl$ (9.6 g, 0.14 mol, 1.5 equiv) and $K_2CO_3$ (7.2 g, 0.07 mol, 1.5 equiv) in $Et_2O$ (60 mL) and $H_2O$ (2 mL) was stirred for about 1 h at room temperature with evolution of $CO_2$ gas. A solution of $Boc_2O$ (20.0 g, 92 mmol) in $Et_2O$ (40 mL) was then added dropwise at 0 °C and the suspension was stirred at room temperature for 12 h. The organic phase was decanted and the solid was washed with $Et_2O$ (30 mL × 2) and the organic layers were combined and concentrated. Recrystallization with a cyclohexane/toluene mixture afforded the desired product.[26]

*General Procedure for the Preparation of N-Hydroxyl Carbamate (ROCONHOH, R = Me, i-Bu, Bn).* *N*-Hydroxyl carbamates were prepared from hydroxylamine with the corresponding chloroformates according to a known procedure. Hydroxylamine hydrochloride (13.9 g, 200 mmol) was added to aqueous solution of NaOH (1.5 M, 160 mL, 240 mmol). The solution was cooled to 0 °C and chloroformate (38 mmol) was added dropwise. Upon the completion of addition, the mixture was warmed up to room temperature and stirred for additional 2 h. The reaction was then acidified with aqueous HCl (6 M) until pH is around 4.5. Then the mixture was extracted with $Et_2O$ (200 mL × 3) and the combined organic layers were washed with brine and dried over anhydrous $Na_2SO_4$. After removal of the solvent in vacuo, the *N*-hydroxyl carbamate was used directly without further purification.[26]

*General Procedure for the Preparation of N-Hydroxyl Carbamate (ROCONHOH, R = Et, n-Bu, n-Penyane, n-Hexyl).* To a flame-dried 100 mL round-bottom flask equipped with a stir bar was added CDI (1.78 g, 11 mmol) in anhydrous THF (30 mL). The flask was cooled to 0 °C and alcohol (10 mmol) was added dropwise. The mixture was stirred for additional 1 h at room temperature and then $NH_2OH\cdot HCl$ (1.04 g, 15 mmol) and imidazole (0.82 g, 12 mmol) were added in one portion. The reaction was monitored by TLC, until the starting material disappeared (about 1 h). Then the mixture was filtered and concentrated in vacuo. The residue was dissolved in EtOAc (40 mL) and washed with aqueous HCl (1 M, 20 mL × 3). The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated to afford the crude product (85−88% yield), which can be used directly for next step.[26]

**General Procedure for the Preparation of *O*-Aroyloxycarbamates (1a).** To a 250 mL flame-dried round-bottom flask equipped with a stir bar, an *N*-hydroxyl *tert*-butyl carbamate (20 mmol, 1.0 equiv), 2-bromobenzoic acid (4.22 g, 21 mmol), and anhydrous $CH_2Cl_2$ (80 mL) were added. The flask was cooled to −15 °C. DCC (4.53 g, 22 mmol, dissolved in 20 mL of anhydrous $CH_2Cl_2$) solution was then added dropwise. The reaction mixture was stirred at the same temperature for additional 30 min until the *N*-hydroxyl carbamate was fully consumed (monitored by TLC). The white precipitate (*N*,*N*′-dicyclohexylurea) was removed by filtration and the filtrate was concentrated in vacuo and dissolved again in $Et_2O$ (30 mL). The solution was cooled to −20 °C for 2 h and filtered again to remove additional precipitate. The organic layer was then concentrated in vacuo and the residue was recrystallized from hexanes and EtOAc to afford corresponding acyloxyl carbamate **1a** as a white solid (yield 90%).[26]



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**General Procedure for the Synthesis of 2-Vinylanilines (3a–3l and 3aa–3ak).** To a solution of **1** (0.5 mmol), $[Pd(DMAP)_2(acac)]_2[V_6O_{11}(OMe)_8]\cdot H_2O$ (0.025 mmol, 5 mol%), styrene (0.6 mmol), and $Cs_2CO_3$ (0.5 mmol) in chlorobenzene (5 mL) in a Schlenk pressure tube (10 mL) under a dry argon atmosphere. The reaction mixture was vigorously stirred at 100 °C for 8–14 h, quenched by ethyl acetate, and purified by silica gel chromatography using a mixture of hexanes and EtOAc to provide the desired **3** (hexane:EtOAc = 10:1 for **3a–3h**, **3aa–3ak**; hexane:EtOAc = 5:1 for **3i**; hexane:EtOAc = 20:1 for **3j–3l**; note: neutral alumina column for **3j–3l**).

*tert-Butyl-(2-styrylphenyl)carbamate (**3a**, Table 2, Entry 1).*[27] White solid (116 mg, 78% yield); mp: 130–132 °C; $R_f$ = 0.43 (hexane:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.78 (d, $J$ = 6.4 Hz, 1H), 7.50 (t, $J$ = 7.6 Hz, 3H), 7.37 (t, $J$ = 7.2 Hz, 2H), 7.30–7.23 (m, 2H), 7.15 (d, $J$ = 16.4 Hz, 1H), 7.15 (t, $J$ = 7.6 Hz, 1H), 6.98 (d, $J$ = 16.4 Hz, 1H), 6.45 (s, 1H), 1.52 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.2, 137.2, 135.4, 132.3, 129.3, 128.8, 128.4, 128.0, 126.9, 126.7, 124.3, 123.6, 122.3, 80.7, 28.4.

*tert-Butyl-(2-(4-methylstyryl)phenyl)carbamate (**3b**, Table 2, Entry 2).* White solid (125 mg, 81% yield); mp: 120–121 °C; $R_f$ = 0.45 (hexane:EtOAc = 10:1); IR (film) 3428, 1733, 1521, 1447, 1359, 1230, 1153, 1050, 806 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80 (d, $J$ = 6.4 Hz, 1H), 7.50 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.43 (d, $J$ = 8.0 Hz, 2H), 7.29–7.25 (m, 1H), 7.20 (d, $J$ = 8.0 Hz, 2H), 7.13–7.09 (m, 2H), 6.97 (d, $J$ = 16.0 Hz, 1H), 6.45 (s, 1H), 2.38 (s, 3H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.1, 138.0, 135.2, 134.3, 132.3, 129.4, 128.1, 126.8, 126.5, 124.1, 122.5, 122.0, 80.6, 28.3, 21.2; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{20}H_{23}NO_2$ 310.1802; found 310.1803.

*tert-Butyl-(2-(4-chlorostyryl)phenyl)carbamate (**3c**, Table 2, Entry 3).* White solid (143 mg, 87% yield); mp: 159–160 °C; $R_f$ = 0.40 (hexane:EtOAc = 10:1); IR (film) 3440, 1701, 1444, 1383, 1162, 1015, 809 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.75 (d, $J$ = 7.2 Hz, 1H), 7.50 (dd, $J$ = 7.6, 1.0 Hz, 1H), 7.44 (d, $J$ = 8.4 Hz, 2H), 7.34 (d, $J$ = 8.8 Hz, 2H), 7.31–7.27 (m, 1H), 7.16–7.11 (m, 2H), 6.94 (d, $J$ = 16.0 Hz, 1H), 6.43 (s, 1H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.2, 135.6, 135.3, 133.6, 130.7, 129.2, 128.9, 128.5, 127.8, 126.7, 124.4, 124.2, 122.6, 80.7, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{19}H_{20}ClNO_2$ 330.1255; found 330.1263.

*tert-Butyl-(2-(4-fluorostyryl)phenyl)carbamate (**3d**, Table 2, Entry 8).* White solid (133 mg, 85% yield); mp: 143–144 °C; $R_f$ = 0.41 (hexane:EtOAc = 10:1); IR (film) 3440, 1653, 1506, 1362, 1227, 1150, 815 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 7.2 Hz, 1H), 7.50–7.49 (m, 3H), 7.30–7.25 (m, 1H), 7.14–7.05 (m, 4H), 6.95 (d, $J$ = 16.4 Hz, 1H), 6.42 (s, 1H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 162.5 (d, $J$ = 251.3 Hz), 153.1, 135.3, 133.3 (d, $J$ = 3.0 Hz), 130.9, 129.3, 128.4, 128.2 (d, $J$ = 8.0 Hz), 126.7, 124.3, 123.3 (d, $J$ = 2.0 Hz), 122.4, 115.6 (d, $J$ = 22.2 Hz), 80.7, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{19}H_{20}FNO_2$ 314.1551; found 314.1559.

*tert-Butyl-(2-(2-chlorostyryl)phenyl)carbamate (**3e**, Table 2, Entry 9).* White solid (122 mg, 74% yield); mp: 111–113 °C; $R_f$ = 0.39 (hexane:EtOAc = 10:1); IR (film) 3414, 2972, 1686, 1459, 1156, 1035, 747 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.79–7.78 (m, 1H), 7.69 (dd, $J$ = 7.6, 1.6 Hz, 1H), 7.55–7.54 (m, 1H), 7.42–7.38 (m, 2H), 7.33–7.28 (m, 2H), 7.26–7.21 (m, 1H), 7.16–7.11 (m, 2H), 6.46 (s, 1H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.1, 135.4, 135.3, 133.5, 129.8, 129.0, 128.9, 128.7, 128.3, 127.2, 126.9, 126.7, 126.4, 124.3, 122.4, 80.7, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{19}H_{20}ClNO_2$ 330.1255; found 330.1264.

*tert-Butyl-(2-(3-chlorostyryl)phenyl)carbamate (**3f**, Table 2, Entry 10).* White solid (135 mg, 82% yield); mp: 138–139 °C; $R_f$ = 0.40 (hexane:EtOAc = 10:1); IR (film) 3411, 1689, 1444, 1165, 1021, 773 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.75 (d, $J$ = 7.6 Hz, 1H), 7.50–7.48 (m, 2H), 7.38–7.36 (m, 1H), 7.31–7.24 (m, 3H), 7.18–7.10 (m, 2H), 6.92 (d, $J$ = 16.0 Hz, 1H), 6.41 (s, 1H), 1.53 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.2, 139.0, 135.4, 134.7, 130.6, 129.9, 129.0, 128.7, 127.8, 126.8, 126.4, 125.1, 124.9, 124.5, 122.6, 80.8, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{19}H_{20}ClNO_2$ 330.1255; found 330.1266.

*tert-Butyl-(2-(4-methoxystyryl)phenyl)carbamate (**3g**, Table 2, Entry 11).* White solid (124 mg, 76% yield); mp: 117–118 °C; $R_f$ = 0.37 (hexane:EtOAc = 10:1); IR (film) 3422, 1639, 1506, 1247, 1156, 956 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.78 (d, $J$ = 6.8 Hz, 1H), 7.48–7.44 (m, 3H), 7.27–7.22 (m, 1H), 7.09 (t, $J$ = 7.6 Hz, 1H), 7.01 (d, $J$ = 16.0 Hz, 1H), 6.94–6.90 (m, 3H), 6.44 (s, 1H), 3.83 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 159.6, 153.1, 135.2, 131.9, 130.0, 129.5, 128.0, 127.9, 126.7, 124.2, 122.0, 121.4, 114.2, 80.6, 55.3, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{20}H_{23}NO_3$ 326.1751; found 326.1748.

*tert-Butyl-(2-(3-phenoxyprop-1-en-1-yl)phenyl)carbamate (**3h**, Table 2, Entry 12).* White solid (127 mg, 78% yield); mp: 65–67 °C; $R_f$ = 0.44 (hexane:EtOAc = 10:1); IR (film) 3437, 1721, 1486, 1221, 1150, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.76 (d, $J$ = 8.0 Hz, 1H), 7.38 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.33–7.24 (m, 3H), 7.07 (t, $J$ = 7.6 Hz, 1H), 6.99–6.95 (m, 3H), 6.81 (d, $J$ = 15.6 Hz, 1H), 6.35 (s, 1H), 6.33–6.26 (m, 1H), 4.72 (dd, $J$ = 5.6, 1.6 Hz, 2H), 1.51 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 158.4, 153.0, 135.2, 129.5, 128.6, 128.3, 127.9, 127.2, 124.1, 122.0, 121.1, 114.8, 80.6, 68.4, 28.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{20}H_{23}NO_3$ 326.1751; found 326.1759.

*Methyl-3-(2-((tert-butoxycarbonyl)amino)phenyl)acrylate (**3i**, Table 2, Entry 13).*[28] White solid (76 mg, 55% yield); mp: 83–85 °C; $R_f$ = 0.33 (hexane:EtOAc = 5:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.84 (d, $J$ = 16.0 Hz, 1H), 7.46 (d, $J$ = 8.0 Hz, 1H), 7.50 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.35 (t, $J$ = 8.0 Hz, 1H), 7.11 (t, $J$ = 8.0 Hz, 1H), 6.54 (s, 1H), 6.38 (d, $J$ = 16.0 Hz, 1H), 3.81 (s, 3H), 1.52 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 167.2, 153.0, 139.6, 136.6, 130.8, 127.1, 126.2, 124.4, 123.0, 120.0, 81.0, 51.8, 28.2.

*tert-Butyl (2-(1-Ethoxyvinyl)phenyl)carbamate (**3j**, Table 2, Entry 14).* Oil (82 mg, 62% yield); $R_f$ = 0.57 (hexane:EtOAc = 20:1); IR (film) 3402, 2987, 1721, 1521, 1439, 1241, 1177, 1038, 765 cm$^{-1}$; $^1$H NMR (700 MHz, $CDCl_3$): $\delta$ 8.08 (d, $J$ = 4.9 Hz, 1H), 7.93 (s, 1H), 7.32 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.31–7.29 (m, 1H), 6.99–6.96 (m, 1H), 4.41 (d, $J$ = 2.8 Hz, 1H), 4.38 (d, $J$ = 2.1 Hz, 1H), 3.96 (q, $J$ = 7.0 Hz, 2H), 1.51 (s, 9H), 1.43 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 160.2, 152.8, 136.3, 129.4, 129.1, 125.9, 122.3, 119.3, 87.4, 80.0, 63.6, 28.3, 14.3; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{15}H_{21}NO_3$ 264.1594; found 264.1595.

*tert-Butyl (2-(1-Isobutoxyvinyl)phenyl)carbamate (**3k**, Table 2, Entry 15).* Oil (116 mg, 80% yield); $R_f$ = 0.58 (hexane:EtOAc = 20:1); IR (film) 3405, 2975, 1721, 1515, 1447, 1162, 1018, 756 cm$^{-1}$; $^1$H NMR (700 MHz, $CDCl_3$): $\delta$ 8.12 (d, $J$ = 7.0 Hz, 1H), 7.92 (s, 1H), 7.33–7.29 (m, 2H), 6.99–6.96 (m, 1H), 4.39 (d, $J$ = 2.8 Hz, 1H), 4.37 (d, $J$ = 2.1 Hz, 1H), 3.66 (d, $J$ = 6.3 Hz, 2H), 2.10 (9, $J$ = 7.0 Hz, 1H), 1.50 (s, 9H), 1.06 (d, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 160.6, 152.7, 136.4, 129.4, 129.3, 126.1, 122.2, 119.1, 87.3, 80.0, 74.6, 28.3, 28.0, 19.5; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{17}H_{25}NO_3$ 292.1907; found 292.1911.

*tert-Butyl (2-(1-Butoxyvinyl)phenyl)carbamate (**3l**, Table 2, Entry 16).* Oil (125 mg, 86% yield); $R_f$ = 0.58 (hexane:EtOAc = 20:1); IR (film) 3405, 2966, 1727, 1518, 1447, 1247, 1153, 1024, 762 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.11 (d, $J$ = 8.0 Hz, 1H), 7.90 (s, 1H), 7.32–7.26 (m, 2H), 6.97 (t, $J$ = 7.6 Hz, 1H), 4.39 (d, $J$ = 2.4 Hz, 1H), 4.37 (d, $J$ = 2.4 Hz, 1H), 3.89 (t, $J$ = 6.4 Hz, 2H), 1.81–1.74 (m, 2H), 1.57–1.52 (m, 2H), 1.51 (s, 9H), 0.99 (t, $J$ = 8.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 160.6, 152.8, 136.3, 129.4, 129.2, 126.0, 122.2, 119.2, 87.2, 80.0, 67.9, 31.0, 28.3, 19.6, 13.9; HRMS (ESI-TOF) $m/z$: $[M+H]^+$ Calcd for $C_{17}H_{25}NO_3$ 292.1907; found 292.1914.

*Benzyl-(2-styrylphenyl)carbamate (**3aa**, Table 3, Entry 1).*[27] White solid (115 mg, 70% yield); mp: 83–85 °C; $R_f$ = 0.43 (hexane:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.82 (s, 1H), 7.53–7.48 (m, 3H), 7.43–7.27 (m, 9H), 7.18–7.12 (m, 2H), 6.99 (d, $J$ = 16.0 Hz, 1H), 6.64 (s, 1H), 5.23 (s, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.8, 136.9, 136.0, 134.7, 132.7, 128.7, 128.6, 128.4, 128.4, 128.4, 128.1, 126.9, 126.7, 124.8, 123.1, 67.2.

*Methyl-(2-styrylphenyl)carbamate (**3ab**, Table 3, Entry 2).*[29] White solid (78 mg, 62% yield); mp: 82–83 °C; $R_f$ = 0.38 (hexane:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.79 (s, 1H), 7.53–7.51 (m, 3H), 7.38 (t, $J$ = 7.2 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz,



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2H), 7.19−7.15 (m, 2H), 7.00 (d, $J$ = 16.0 Hz, 1H), 6.61 (s, 1H), 3.80 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 154.5, 136.9, 134.8, 132.7, 129.5, 128.8, 128.4, 128.1, 126.9, 126.7, 124.7, 123.2, 122.4, 52.5.

*Ethyl-(2-styrylphenyl)carbamate (**3ac**, Table 3, Entry 3).*[27] White solid (93 mg, 70% yield); mp: 66−71 °C; $R_f$ = 0.40 (hexane:EtOAc = 10:1); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.79 (s, 1H), 7.52−7.50 (m, 3H), 7.39−7.36 (m, 2H), 7.31−7.27 (m, 2H), 7.18−7.12 (m, 2H), 6.99 (d, $J$ = 16.0 Hz, 1H), 6.58 (s, 1H), 4.23 (q, $J$ = 7.2 Hz, 2H), 1.31 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 154.0, 137.0, 134.9, 132.6, 129.3, 128.8, 128.4, 128.1, 126.9, 126.7, 124.6, 123.3, 122.3, 61.4, 14.5.

*Isopropyl-(2-styrylphenyl)carbamate (**3ad**, Table 3, Entry 4).* White solid (94 mg, 67% yield); mp: 76−77 °C; $R_f$ = 0.41 (hexane:EtOAc = 10:1); IR (film) 3411, 2978, 1689, 1444, 1035, 750 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.83 (s, 1H), 7.52 (t, $J$ = 7.2 Hz, 3H), 7.39 (t, $J$ = 7.6 Hz, 2H), 7.32−7.28 (m, 2H), 7.19−7.12 (m, 2H), 7.00 (d, $J$ = 16.0 Hz, 1H), 6.53 (s, 1H), 5.05 (sep, $J$ = 6.4 Hz, 1H), 1.31 (d, $J$ = 6.0 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.6, 137.0, 135.1, 132.6, 129.1, 128.7, 128.4, 128.1, 126.9, 126.7, 124.4, 123.4, 122.1, 69.0, 22.1; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{18}H_{19}NO_2$ 282.1489; found 282.1488.

*Butyl-(2-styrylphenyl)carbamate (**3ae**, Table 3, Entry 5).* White solid (108 mg, 73% yield); mp: 47−49 °C; $R_f$ = 0.43 (hexane:EtOAc = 10:1); IR (film) 3428, 2955, 1692, 1450, 1218, 1044, 753 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.79 (s, 1H), 7.53−7.51 (m, 3H), 7.40−7.36 (m, 2H), 7.32−7.27 (m, 2H), 7.18−7.12 (m, 2H), 7.00 (d, $J$ = 16.4 Hz, 1H), 6.55 (s, 1H), 4.19 (t, $J$ = 6.4 Hz, 2H), 1.70−1.63 (m, 2H), 1.46−1.37 (m, 2H), 0.97−0.93 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 154.1, 137.0, 134.9, 132.6, 129.0, 128.7, 128.4, 128.1, 126.9, 126.7, 124.6, 123.3, 65.3, 31.0, 19.1, 13.7; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{19}H_{21}NO_2$ 296.1645; found 296.1649.

*Isobutyl-(2-styrylphenyl)carbamate (**3af**, Table 3, Entry 6).* White solid (97 mg, 66% yield); mp: 70−72 °C; $R_f$ = 0.44 (hexane:EtOAc = 10:1); IR (film) 3446, 2955, 1704, 1453, 1218, 1038, 759 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.79 (s, 1H), 7.52 (d, $J$ = 7.6 Hz, 3H), 7.39 (t, $J$ = 7.2 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz, 2H), 7.20−7.13 (m, 2H), 7.00 (d, $J$ = 16.0 Hz, 1H), 6.56 (s, 1H), 3.97 (d, $J$ = 6.8 Hz, 2H), 1.99 (sep, $J$ = 6.8 Hz, 1H), 0.97 (d, $J$ = 6.4 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 154.2, 137.0, 134.9, 132.6, 128.8, 128.4, 128.1, 126.9, 126.7, 124.6, 123.3, 71.6, 27.9, 19.1; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{19}H_{21}NO_2$ 296.1645; found 296.1647.

*Pentyl-(2-styrylphenyl)carbamate (**3ag**, Table 3, Entry 7).* White solid (97 mg, 63% yield); mp: 76−78 °C; $R_f$ = 0.45 (hexane:EtOAc = 10:1); IR (film) 3423, 2955, 1671, 1530, 1444, 1032, 765 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.80 (s, 1H), 7.54−7.51 (m, 3H), 7.41−7.31 (m, 2H), 7.32−7.28 (m, 2H), 7.19−7.13 (m, 2H), 7.00 (d, $J$ = 16.0 Hz, 1H), 6.56 (s, 1H), 4.18 (t, $J$ = 6.8 Hz, 2H), 1.72−1.65 (m, 2H), 1.39−1.34 (m, 4H), 1.93−0.89 (m, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 154.1, 137.0, 134.9, 132.6, 129.5, 128.7, 128.4, 128.1, 126.9, 126.7, 124.6, 123.3, 122.3, 65.6, 28.6, 28.0, 22.3, 13.9; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{20}H_{23}NO_2$ 310.1802; found 310.1804.

*Hexyl-(2-styrylphenyl)carbamate (**3ah**, Table 3, Entry 8).* White solid (99 mg, 61% yield); mp: 72−74 °C; $R_f$ = 0.45 (hexane:EtOAc = 10:1); IR (film) 3414, 2949, 1659, 1450, 1047, 753 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.73 (s, 1H), 7.44 (d, $J$ = 7.6 Hz, 3H), 7.31 (t, $J$ = 7.6 Hz, 2H), 7.25−7.20 (m, 2H), 7.11−7.05 (m, 2H), 6.93 (d, $J$ = 16.4 Hz, 1H), 6.48 (s, 1H), 4.10 (t, $J$ = 6.8 Hz, 2H), 1.64−1.57 (m, 2H), 1.31−1.89 (m, 6H), 0.82 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 153.1, 135.9, 133.9, 131.5, 127.7, 127.4, 127.0, 125.9, 125.6, 123.5, 122.3, 121.2, 64.6, 30.4, 27.8, 24.5, 21.5, 12.9; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{21}H_{25}NO_2$ 324.1958; found 324.1964.

*tert-Butyl-(3-styrylphenyl)carbamate (**3ai**, Table 3, Entry 9).* White solid (109 mg, 74% yield); mp: 123−125 °C; $R_f$ = 0.38 (hexane:EtOAc = 10:1); IR (film) 2927, 1701, 1530, 1444, 1235, 1156, 1050, 1009 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.62 (s, 1H), 7.50 (d, $J$ = 8.0 Hz, 2H), 7.36 (t, $J$ = 8.0 Hz, 2H), 7.29−7.24 (m, 2H), 7.20−7.17 (m, 2H), 7.13 (d, $J$ = 16.4 Hz, 1H), 7.08 (d, $J$ = 16.4 Hz, 1H), 6.49 (s, 1H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 152.7, 138.7, 138.2, 137.2, 129.2, 129.1, 128.6, 128.4, 127.6, 126.5, 121.3, 117.7, 116.3, 80.6, 28.3; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{19}H_{21}NO_2$ 296.1645; found 296.1654.

*tert-Butyl-(3-(4-methylstyryl)phenyl)carbamate (**3aj**, Table 3, Entry 10).* White solid (116 mg, 75% yield); mp: 76−78 °C; $R_f$ = 0.40 (hexane:EtOAc = 10:1); IR (film) 3440, 1701, 1439, 1162, 1041, 962, 876 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.60 (s, 1H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.28−7.24 (m, 1H), 7.19−7.16 (m, 4H), 7.09 (d, $J$ = 16.4 Hz, 1H), 7.02 (d, $J$ = 16.0 Hz, 1H), 6.50 (s, 1H), 2.36 (s, 3H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 152.7, 138.7, 138.4, 137.6, 134.4, 129.4, 129.1, 129.0, 127.4, 126.4, 121.2, 117.5, 116.2, 80.6, 28.38, 21.2; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{20}H_{23}NO_2$ 310.1802; found 310.1810.

*tert-Butyl-(3-(4-chlorostyryl)phenyl)carbamate (**3ak**, Table 3, Entry 11).* White solid (125 mg, 76% yield); mp: 148−150 °C; $R_f$ = 0.35 (hexane:EtOAc = 10:1); IR (film) 3434, 1721, 1450, 1380, 1153, 1026, 809 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.65 (s, 1H), 7.43 (d, $J$ = 8.4 Hz, 2H), 7.31 (d, $J$ = 8.4 Hz, 2H), 7.29−7.25 (m, 1H), 7.17 (t, $J$ = 7.6 Hz, 2H), 7.05 (s, 2H), 6.49 (s, 1H), 1.54 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 152.7, 138.8, 137.9, 135.7, 133.2, 129.2, 129.1, 128.8, 127.8, 127.7, 121.4, 117.9, 116.3, 80.6, 28.3; HRMS (ESI-TOF) $m/z$: [M+H]$^+$ Calcd for $C_{19}H_{20}ClNO_2$ 330.1255; found 330.1269.

**General Procedure for Preparation of 2-Substituted Indole 4a.** To a solution of substrate **3a** (0.147 g, 0.5 mmol) in $CH_2Cl_2$ (1.0 mL) was added NIS (0.173 g, 1.0 mmol) under air. The resulting mixture was stirred at rt for the 50 h, then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 10:1 as an eluent) to give the corresponding product **4a**.

*tert-Butyl 2-Phenyl-1H-indole-1-carboxylate (**4a**).*[22] White solid (73 mg, 50% yield); mp: 76−77 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.21 (d, $J$ = 8.4 Hz, 1H), 7.54 (d, $J$ = 7.6 Hz, 1H), 7.43−7.30 (m, 6H), 7.26−7.22 (m, 1H), 6.55 (s, 1H), 1.30 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 150.2, 140.5, 137.4, 135.0, 129.2, 128.7, 127.8, 127.5, 124.3, 122.9, 120.4, 115.2, 109.9, 83.4, 27.5.

**General Procedure for Preparation of *t*-Butyl (*Z*)-(2-Styrylphenyl)carbamate 5a.** To a solution of substrate **3a** (0.147 g, 0.5 mmol) in $CH_3CN$ (1.0 mL) under air. The resulting mixture was stirred at rt for the 36 h under the high pressure mercury lamp (500 W) as the light resource, then the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:EtOAc = 20:1 as an eluent) to give the corresponding product **5a**.[23a] White solid (66 mg, 90% yield); mp: 77−79 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.00 (d, $J$ = 8.4 Hz, 1H), 7.26 (t, $J$ = 8.8 Hz, 1H), 7.19−7.12 (m, 6H), 6.97 (t, $J$ = 7.6 Hz, 1H), 6.76 (d, $J$ = 12.0 Hz, 1H), 6.53 (d, $J$ = 12.0 Hz, 1H), 6.52 (s, 1H), 1.42 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 152.8, 136.0, 135.6, 133.3, 129.1, 128.8, 128.4, 127.7, 126.7, 125.6, 123.3, 119.2, 80.4, 28.3.

**General Procedure for 6a.** To a solution of **1a** (0.158 g, 0.5 mmol), catalyst **A** (0.041 g, 0.025 mmol, 5 mol%), styrene (0.062 g, 0.6 mmol), and $Cs_2CO_3$ (0.1629 g, 0.5 mmol) in chlorobenzene (5 mL) in a Schlenk pressure tube (10 mL) under a dry argon atmosphere. The reaction mixture was vigorously stirred at 100 °C, detected the reaction by TLC every 10 min we detected the **6a** first, when the reaction was stirred at 100 °C for 1 h, **1a** was consumed completely and a few of **3a** was detected, most of the intermediate **6a** was detected, quenched by ethyl acetate, and purified by silica gel chromatography using a mixture of hexanes and EtOAc (hexane:EtOAc = 10:1 as an eluent) to provide the intermediate product **6a** (65 mg, 48%).

*tert-Butyl (2-Bromophenyl)carbamate (**6a**).*[23a] Colorless oil; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.17 (dd, $J$ = 8.3, 1.1 Hz, 1H), 7.51 (dd, $J$ = 8.0, 1.5 Hz, 1H), 7.33−7.23 (m, 1H), 7.03 (s, 1H), 6.93−6.89 (m, 1H), 1.56 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ 152.3, 136.3, 132.2, 128.2, 123.8, 120.0, 112.3, 81.0, 28.2.

## ■ ASSOCIATED CONTENT

### Supporting Information

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$^{1}H$ and $^{13}C$ NMR spectra of all the compounds **3** (PDF)

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### Notes

The authors declare no competing financial interest.

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