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# Regio- and Stereoselective Olefination of Phenol Carbamates through C–H Bond Functionalization

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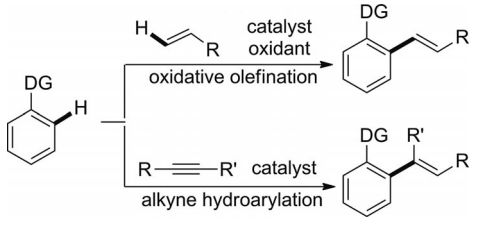
Two pathways that can be used to access *ortho*-olefinated phenol carbamate, including a ruthenium(II)-catalyzed oxidative olefination of phenol carbamate with acrylates and a rhodium(III)-catalyzed alkyne hydroarylation of phenol carbamate with internal alkynes through direct C–H activation, are reported. Both reactions afford substituted alkenes in a highly regio- and stereoselective manner.

## Introduction

The direct functionalization of C–H bonds catalyzed by transition-metal complexes allows the use of less expensive and more readily available starting materials for the construction of complex products.[1] Among these reactions, new carbon–carbon bonds can be formed through direct C–H transformation.[2] Of these processes, catalytic oxidative olefination and alkyne hydroarylation of aryl C–H bonds are two important methods for the synthesis of substituted alkenes in an atom- and step-economic fashion (Scheme 1).




Scheme 1. Catalytic oxidative olefination and alkyne hydroarylation of aryl C–H bonds to synthesize substituted alkenes.

As an attractive alternative to traditional Heck coupling reactions, the catalytic oxidative alkenylation method (known as the Fujiwara–Moritani reaction[3]) is a more efficient and greener process. Palladium[4] complexes were the most frequently used catalysts for this useful transformation. Later, rhodium-complex-catalyzed oxidative olefinations were independently developed by the research groups of Satoh and Miura,[5] Glorius,[6] Ellmann,[7] Chang,[8] Li,[9] Liu,[10] Loh,[11] and Zhu.[12] Although ruthenium complexes have also been reported to catalyze this type of reaction,[13] the successful applications of less-expensive ruthenium(II) catalysts for the oxidative olefination of arenes were initiated just one year ago. The groups of Satoh and Miura,[14] Ackermann,[15] Bruneau and Dixneuf,[16] and Jeganmohan[17] have shown that use of the [{$RuL_2$(*p*-cymene)}$_2$] (L = Cl or OAc) catalyst allows the oxidative coupling of aromatic acids, aryl ketones, *N*-arylpyrazoles, anilides, amides, aromatic aldehydes, and aromatic esters with olefins by using copper acetate as oxidant. Moreover, we have reported the dehydrogenative alkenylation of *N*-methoxybenzamides with styrene and acrylates in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] as catalyst using CONH(OMe) as an oxidizing directing group.[18] On the other hand, hydroarylation reactions of internal alkynes is a green pathway for redox-neutral olefination of aryl C–H bonds. In this process, no oxidant is needed, and trisubstituted olefin products are formed. Although a variety of transition-metal complexes, such as palladium,[19] rhodium,[20] iridium,[21] rhenium,[22] nickel,[23] cobalt,[24] and ruthenium[25] have been used to catalyze this type of reaction, several issues remain to be addressed such as the limited substrate scope and the regio- and stereoselectivity of the reaction.

The orientation of the directing group was considered useful for controlling the regioselectivity in C–H activation. Aryl carbamate substrates have been widely used in cross-coupling reactions because of their ease of preparation and good stability.[26] However, these substrates have been less well explored as directing groups in C–H bond activation reactions.[27] In a continuation of our interest in transition-metal-catalyzed C–H functionalization,[28] we here disclose

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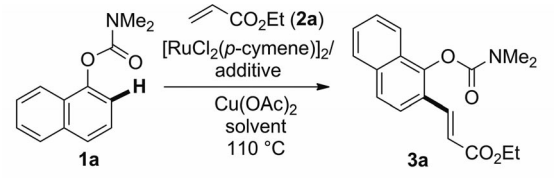
our development of the *ortho*-olefination of carbamate-protected phenols through (a) [{$RuCl_2$(*p*-cymene)}$_2$]/$AgSbF_6$-catalyzed oxidative coupling of phenol carbamate with acrylates,[29] and (b) [Cp*$RhCl_2$]$_2$/$AgSbF_6$-catalyzed alkyne hydroarylation of phenol carbamate with internal alkynes. To our delight, both reactions afforded substituted alkenes in a highly regio- and stereoselective manner.

## Results and Discussion

At the outset of our investigations, the reaction of naphthalen-1-yl dimethylcarbamate (**1a**) with ethyl acrylate (**2a**) was examined as a model reaction (Table 1). After many trials,[30] we found that treatment of **1a** (1.0 equiv.) with **2a** (2.0 equiv.) in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol-%), $AgSbF_6$ (20 mol-%), and $Cu(OAc)_2$ (2.0 equiv.) in tetrahydrofuran (THF) at 110 °C for 30 h gave the desired Heck-type product **3a** in 85% isolated yield with excellent (*E*) stereoselectivity (Table 1, Entry 7). The structure of **3a**, which was confirmed by $^1$H and $^{13}$C NMR spectroscopy and mass spectrometry, is consistent with those reported previously.[11] Among the tested solvents, THF was found to be optimal. Other solvents, such as 2-methyl-2-butanol (*tert*-AmOH), 1,2-dimethoxyethane (DME), and dioxane gave lower yields, whereas $CH_3CN$, *N*,*N*-dimethylformamide (DMF), and $CH_3OH$ completely inhibited the reaction (Table 1, Entries 1–6). Control experiments showed that the absence of either catalyst or silver salt resulted in complete inactivity of the catalytic reaction (Table 1, Entries 8–10).

Table 1. Optimization of ruthenium-catalyzed oxidative C–H olefination of **1a** with acrylic esters.[a]




| Entry | Additive (20mol%) | Solvent | **3a** (%)[b] |
|---|---|---|---|
| 1 | $AgSbF_6$ | *tert*-AmylOH | 30 |
| 2 | $AgSbF_6$ | DME | 69 |
| 3 | $AgSbF_6$ | $CH_3CN$ | 0 |
| 4 | $AgSbF_6$ | DMF | 0 |
| 5 | $AgSbF_6$ | $CH_3OH$ | 0 |
| 6 | $AgSbF_6$ | dioxane | 81 |
| 7 | $AgSbF_6$ | THF | 85 |
| 8[c] | $AgSbF_6$ | THF | 0 |
| 9 | $NH_4PF_6$ | THF | 0 |
| 10 | none | THF | 0 |

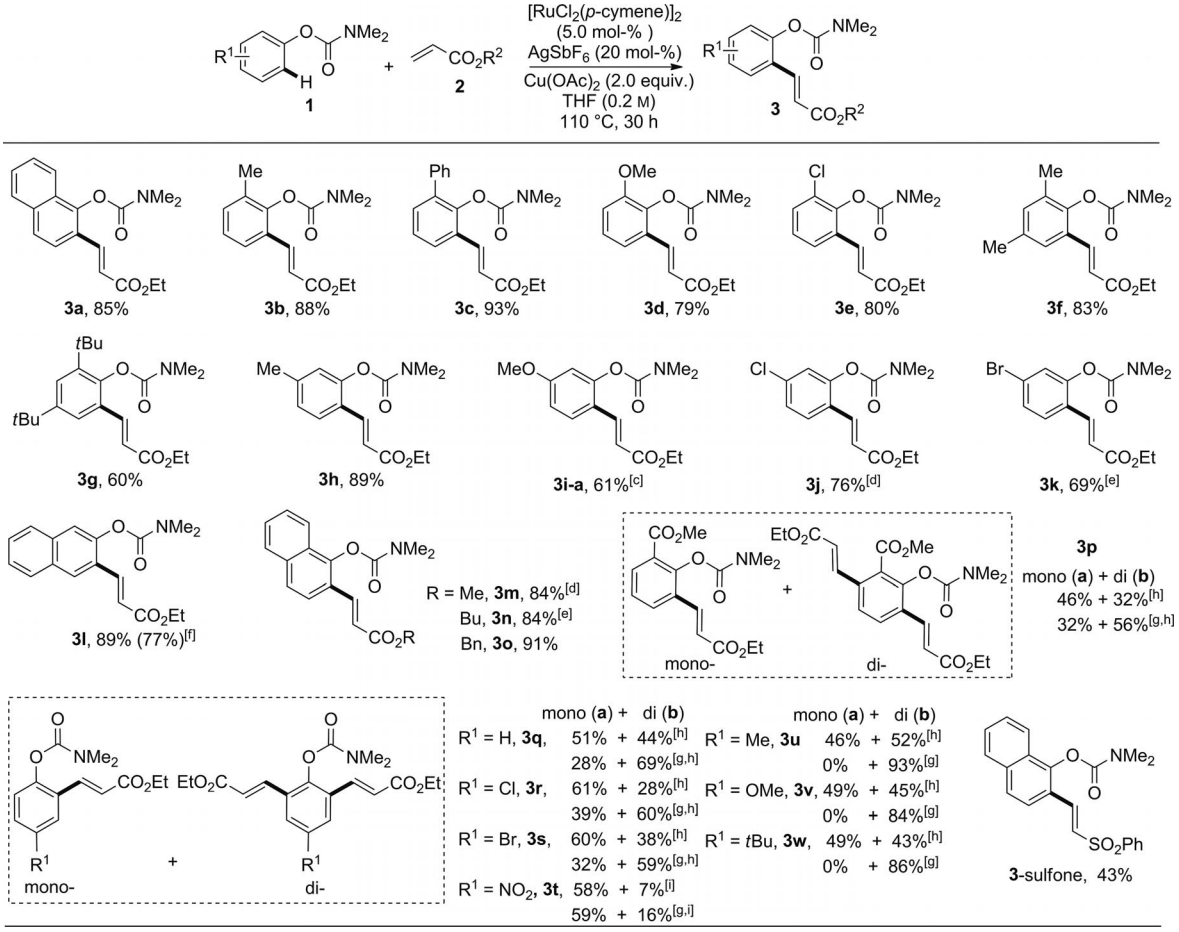
[a] Reaction conditions: carbamate (0.4 mmol), ethyl acrylate (0.8 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol-%), $Cu(OAc)_2$ (2.0 equiv.), solvent (2.0 mL), 110 °C, 30 h, under Ar. [b] Isolated yield. [c] No [$RuCl_2$(*p*-cymene)]$_2$.

We then studied the reactions of various aryl carbamates **1** with **2a** under the optimized reaction conditions; Table 2 outlines the scope of the reaction. Phenyl carbamates containing either electron-donating or -withdrawing groups participated well in this reaction and gave the corresponding alkene derivatives (**3a**–**l** and **3p**–**w**) in good to excellent yields. Substrates bearing *ortho*-substituted groups did not affect the reactions and underwent the desired oxidative coupling with **2a** to yield **3b**–**g**. The reactions exhibited high regioselectivity with C–H olefination at the sterically less hindered position when *meta*-substituted substrates were used (**3h**–**l**). It was interesting to find that in the case of *meta*-OMe substituted substrate **1i**, a minor amount of diolefinated product **3i-b** was also obtained in 29% yield, suggesting the strong electronic effect of the substrate **1i**. Similar results were also observed in Rh-catalyzed processes.[11] When substrate **1p**, containing both carbamate and carboxylate groups, was employed in the reaction, a mixture of mono- and diolefinated products was afforded, with monoolefination occurring at the *ortho* position of the carbamate group. This result suggests that carbamate is a more efficient C–H-activation-directing group in the current $Ru^{II}$-catalyzed system. It is noteworthy that halide functional groups were compatible in the present catalytic reaction (*o*-Cl for **3e**, *m*-Cl for **3j**, *m*-Br for **3k**, *p*-Cl for **3r**, and *p*-Br for **3s**), which offers the opportunity for further coupling to afford more complex molecules. However, although *o*-Br-substituted carbamate produced the dehalogenated complex in our Ru-catalyzed system,[31] it was tolerated in the Rh-catalyzed reactions.[11] Under the standard reaction conditions, the *para*-substituted substrates were inclined to generate a mixture of mono- and diolefinated products (**3q**–**w**). Interestingly, substrates containing an electron-donating group at the *para*-position led to complete formation of the diolefinated products by using twofold excess of catalyst and acrylate (**3u**–**w**), whereas electron-neutral and -poor substrates gave predominantly the diolefinated products (**3q**–**s**) even when the amounts of catalyst and acrylate were doubled. The *p*-$NO_2$-substituted substrate, which exhibited low reactivity in the Rh-catalyzed process,[10] afforded monoolefinated compound **3t-a** as the predominant product in our reaction system. Moreover, various acrylates, such as methyl acrylate, *n*-butyl acrylate, and benzyl acrylate, were smoothly incorporated to produce the corresponding products **3m**–**o** in good to excellent yield. Other alkenes bearing electron-withdrawing groups were also tested: *N*,*N*-dimethylacrylamide and acrylonitrile showed very low reactivity, whereas phenyl vinyl sulfone could be used as substrate to yield the **3**-sulfone in 43% yield (Table 2). Disappointingly, styrene failed to react with phenyl carbamates under these reaction conditions. It also needs to be pointed out that the scope of the method includes alkenyl carbamates derived from α-tetralone, although the desired olefinated products **3x**–**z** were isolated in moderate yields (Scheme 2).

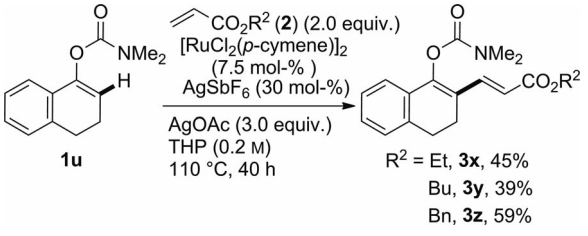
Experiments were conducted to examine the working mode of the reactions. When the reaction of **1a** was carried out in $CD_3OD$ (2.0 mL) or a mixed solvent system of THF (2.0 mL)/$D_2O$ (0.5 mL), 8 and 9% deuterium incorporation was detected at the *ortho* position of the recovered starting

Table 2. Results of ruthenium-catalyzed oxidative C–H olefination with acrylic esters.[a,b]

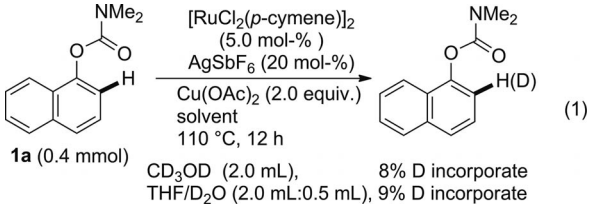



[a] Reaction conditions: carbamate (0.4 mmol), ethyl acrylate (0.8 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol-%), $Cu(OAc)_2$ (2.0 equiv.), THF (2.0 mL), 110 °C, 30 h, under Ar. [b] Isolated yield. [c] The diolefinated product **3i-b** was also isolated in 29% yield. [d] 36 h. [e] 48 h. [f] The data in parentheses refers to the yield of **3l** performed on 3.0 mmol scale. [g] Reaction conditions: acrylate (5.0 equiv.), [$RuCl_2$(*p*-cymene)]$_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), THF (0.2 M), 110 °C, 60 h. [h] The mono- and diolefinated compounds were isolated separately. [i] The mono- and diolefinated compounds were isolated as an inseparable mixture, and the ratio of the two species was determined by $^1$H NMR spectroscopy.



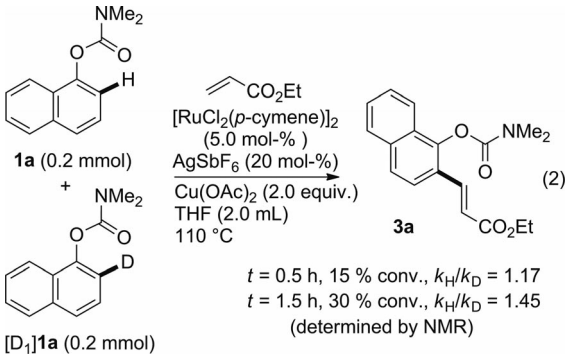

Scheme 2. Results of ruthenium-catalyzed oxidative C–H olefination of 3,4-dihydronaphthalen-1-yl dimethylcarbamate (**1u**) with acrylate. Reagents and conditions: carbamate **1u** (0.4 mmol), ethyl acrylate (0.8 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (7.5 mol-%), $AgSbF_6$ (30 mol-%), AgOAc (3.0 equiv.), THP (2.0 mL), 110 °C, 40 h, under Ar.

material **1a**, respectively [Equation (1)]. This fact suggests that, under the reaction conditions, C–H activation is a reversible but slow process. Moreover, a kinetic isotope effect (KIE) with values of $k_H/k_D$ = 1.17 (at 15% conversion) and 1.45 (at 30% conversion) was observed in the intermolecular isotopic study [Equation (2)].[32]

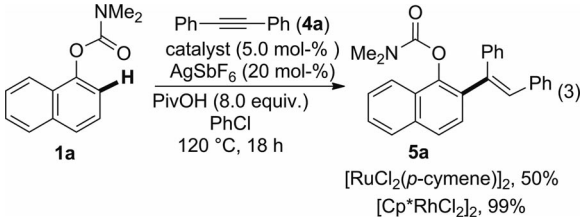



Subsequently, we also explored the catalytic alkyne hydroarylation reaction of **1a** with internal alkynes to synthesize more substituted alkenes. After many optimized experiments,[30] we found that [{$RuCl_2$(*p*-cymene)}$_2$]/$AgSbF_6$ exhibited moderate catalytic activity in the model reaction of **1a** with diphenylacetylene (**4a**) [50% isolated yield of **5a**, Equation (3)]. To our delight, almost quantitative isolated yields were achieved when [Cp*$RhCl_2$]$_2$/$AgSbF_6$ was chosen as catalyst [Equation (3)]. The reaction proceeded with high

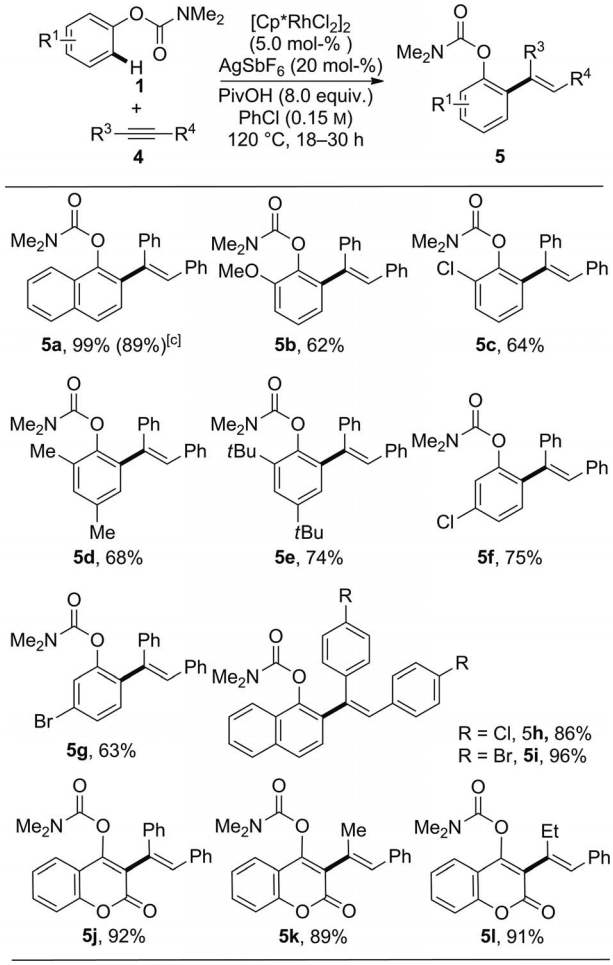



regio- and stereoselectivity, which was confirmed by single-crystal X-ray diffraction analysis of compound **5a** (Figure 1). Notably, control experiments showed that the use of $AgSbF_6$ and PivOH is essential for the success of the reaction.




As shown in Table 3, hydroarylation of various aryl carbamates with diphenylacetylene was examined under similar reaction conditions. It was clear that the electronic nature of the substituents on the aryl carbamates had no significant effect on the reactivity, and **5b**–**g** were obtained in 62–75% isolated yields with excellent (*E*) stereoselectivity. The halide functional groups were again well tolerated (*o*-Cl for **5c**, *m*-Cl for **5f**, and *m*-Br for **5g**) in this catalytic system. In addition, the electron-deficient tolane derivatives, bis(4-chlorophenyl)acetylene (**4b**) and bis(4-bromophenyl)acetylene (**4c**), were good candidates for this reaction, which coupled with **1a** to form the corresponding hydroarylation

Table 3. Results of rhodium-catalyzed alkyne hydroarylation reaction with internal alkynes.[a,b]




[a] Reaction conditions: carbamate **1** (0.3 mmol), ethyl acrylate (0·mmol), PivOH (2.4 mmol), $[Cp^*RhCl_2]_2$ (5.0 mol-%), $AgSbF_6$ (20.0 mol-%), PhCl (2.0 mL), 120 °C, 18–30 h, under Ar. [b] Isolated yield. [c] The data in parentheses refers to the yield of **5a** conducted on 3.0 mmol scale.

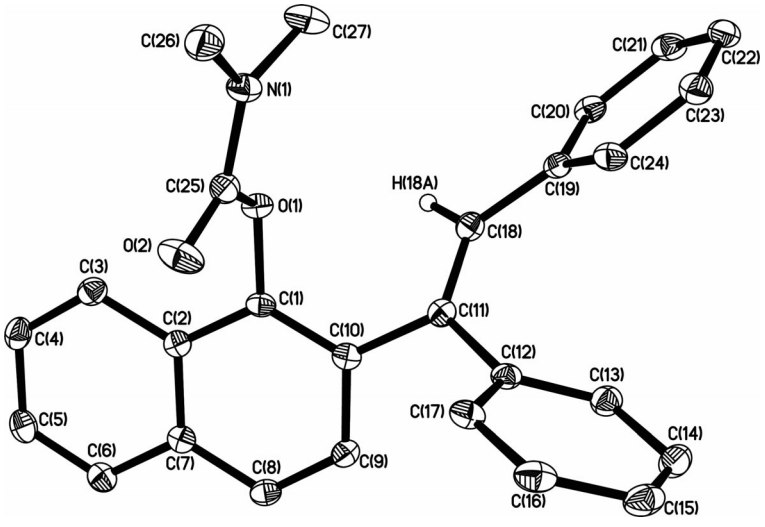



Figure 1. ORTEP representation of compound **5a**; thermal ellipsoids are set at 30% probability. Hydrogen atoms except H(18A) have been omitted for clarity.

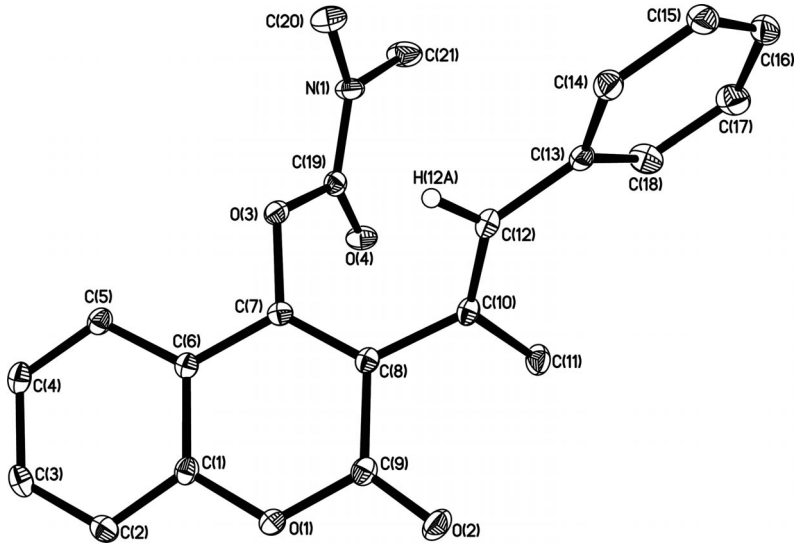
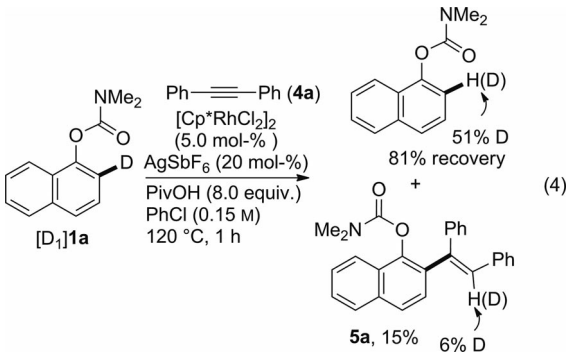



Figure 2. ORTEP representation of compound **5k**; thermal ellipsoids are set at 30% probability. Hydrogen atoms except H(12A) have been omitted for clarity.

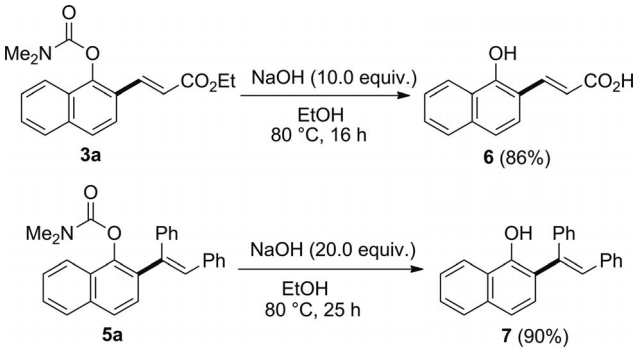
products **5h** and **5i** in 86 and 96% yield, respectively. This protocol could also be applied to carbamate-protected 4-hydroxycoumarin, and the desired products **5j**–**l** were isolated in high yield. It is important to note that when unsymmetrical (alkyl)(phenyl)acetylenes 1-phenylpropyne (**4d**) and 1-phenylbutyne (**4e**) were applied, **5k** and **5l** were isolated as the only regio- and stereoisomers. The structure of compound **5k** was confirmed by single-crystal X-ray diffraction analysis (Figure 2).

In the rhodium-catalyzed alkyne hydroarylation reaction, only very low deuterium incorporation (6%) in the product and a decrease in deuterium incorporation (from 95 to 51%) in the starting material were detected by $^1$H NMR spectroscopy when isotopically labeled substrate [$D_1$]**1a** was employed in the reaction for 1 h [Equation (4)]. The former result excludes the possibility of an oxidative insertion reaction pathway, which should retain deuterium incorporation in the final product. The latter indicates an equilibrium between metalation and proto-demetalation before reaction with the alkyne. These findings are consistent with those found by Schipper et al.[20a] The addition of PivOH is essential for the final protonolysis, which yields the product and regenerates the catalyst.[20a]




(4)

Finally, both reactions were conducted on a large scale with good performance: 3.0 mmol of naphthalen-2-yl dimethylcarbamate (**1l**) afforded **3l** in 77% yield by using the ruthenium(II)-catalyzed oxidative olefination method (Table 2), and naphthalen-1-yl dimethylcarbamate (**1a**) yielded **5a** in 89% yield by using the rhodium(III)-catalyzed alkyne hydroarylation method (Table 3). Moreover, as a protecting group for the phenol derivatives, the carbamate directing group could be easily removed (Scheme 3), which highlights the potential of employing carbamate as a directing group.




Scheme 3. Removal of the carbamate group.

## Conclusions

We have developed two pathways that can be used to access *ortho*-olefinated phenyl carbamates, including a ruthenium(II)-catalyzed oxidative olefination of phenyl carbamate with acrylates, and a rhodium(III)-catalyzed alkyne hydroarylation of phenyl carbamate with internal alkynes through direct C–H activation. Both reactions are highly regio- and stereoselective. Considering that carbamates are generally used as a protecting group for phenol derivatives, these reactions are likely to be useful for the preparation of organic synthetic scaffolds such as substituted phenols or substituted alkenes.

## Experimental Section

**Analytical Methods:** All the reactions were carried out under argon by using standard Schlenk techniques. $^1$H (300 or 400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded with Bruker AV300 or AV400 NMR spectrometers with $CDCl_3$ or [$D_6$]DMSO as solvent. Chemical shifts of $^1$H and $^{13}$C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and chemical shifts are given on the TMS scale ($CDCl_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.00 ppm; [$D_6$]DMSO: $\delta_H$ = 2.50 ppm, $\delta_C$ = 39.52 ppm). All coupling constants (*J* values) are reported in Hertz [Hz]. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). IR spectra were recorded as KBr disks with a Nicolet 380 FTIR spectrometer. EI mass spectra and HRMS data were recorded with Thermo Finnigan TRACE DSQ and Varian 7.0 T FTICR mass spectrometers, respectively.

**Preparation of Chemicals:** [{$RuCl_2$(*p*-cymene)}$_2$] was prepared from $RuCl_3 \cdot xH_2O$ according to a literature procedure.[33] All other reagents were used as received from commercial sources. Unless otherwise noted below, all other compounds have been reported in the literature or are commercially available from Alfa Aesar China (Tianjin) Chemical Co., Ltd. without any further purification. The phenyl carbamate substrates were prepared according to a described procedure.[34]

**General Procedure for the $Ru^{II}$-Catalyzed Olefination of Phenyl Carbamate Derivatives (General Procedure A):** A mixture of **1** (0.40 mmol, 1.0 equiv.), [$RuCl_2$(*p*-cymene)]$_2$ (12.3 mg, 0.020 mmol, 5.0 mol-%), $AgSbF_6$ (27.5 mg, 0.080 mmol, 20 mol-%), and $Cu(OAc)_2$ (145.3 mg, 0.80 mmol, 2.0 equiv.) was weighted in a Schlenk tube equipped with a stir bar. Anhydrous THF (2.0 mL) was added followed immediately by alkene **2** (0.80 mmol, 2.0 equiv.) and the mixture was stirred at 110 °C under Ar for 30 h. The reaction mixture was cooled to room temp. and diluted with $CH_2Cl_2$ and transferred to a round-bottomed flask. Silica was added to the flask, and volatiles were evaporated under reduced pressure. Purification was performed by flash column chromatography on silica gel.

**Ethyl (*E*)-3-[1-(Dimethylcarbamoyloxy)naphthalen-2-yl]acrylate (3a):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as an off-white solid (106.6 mg, 85%) from naphthalen-1-yl dimethylcarbamate (**1a**; 0.40 mmol, 86.1 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.98 (d, *J* = 16.0 Hz, 1 H), 7.88–7.82 (m, 2 H), 7.73–7.68 (m, 2 H), 7.55–7.50 (m, 2 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 4.28 (q, *J* = 7.1 Hz, 3 H), 3.36 (s, 3 H), 3.10 (s, 3 H), 1.35 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.8, 154.2, 146.6, 138.0, 135.2, 127.8, 127.3, 127.0, 126.1, 123.9, 122.7, 122.1, 119.8, 60.4, 36.9, 36.6, 14.2 (one signal missing due to overlap) ppm. MS (EI): calcd. for $C_{18}H_{19}NO_4$ [$M^+$] 313.13; found 313.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-3-methylphenyl]acrylate (3b):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (97.8 mg, 88%) from *o*-tolyl dimethylcarbamate (**1b**; 0.40 mmol, 71.7 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.77 (d, *J* = 16.1 Hz, 1 H), 7.45 (d, *J* = 7.6 Hz, 1 H), 7.22 (d, *J* = 7.3 Hz, 1 H), 7.12 (t, *J* = 7.6 Hz, 1 H), 6.40 (d, *J* = 16.1 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.18 (s, 3 H), 3.02 (s, 3 H), 2.19 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.7, 153.7, 148.7, 138.5, 132.6, 131.8, 127.8, 125.6, 124.8, 119.6, 60.2, 36.7, 36.3, 16.1, 14.1 ppm. MS (EI): calcd. for $C_{15}H_{19}NO_4$ [$M^+$] 277.13; found 277.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)biphenyl-3-yl]acrylate (3c):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (126.4 mg, 93%) from biphenyl-2-yl dimethylcarbamate (**1c**; 0.40 mmol, 96.5 mg, 1.0 equiv.) according to the General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.81 (d, *J* = 16.1 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.37–7.23 (m, 7 H), 6.45 (d, *J* = 16.1 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 2.89 (s, 3 H), 2.75 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.7, 153.7, 147.3, 138.5, 137.3, 136.5, 132.3, 128.8, 128.7, 128.0, 127.4, 126.3, 125.9, 120.1, 60.4, 36.6, 36.2, 14.2 ppm. MS (EI): calcd. for $C_{20}H_{21}NO_4$ [$M^+$] 339.15; found 339.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-3-methoxyphenyl]acrylate (3d):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5 to 1:2) as an off-white solid (92.8 mg, 79%) from 2-methoxyphenyl dimethylcarbamate (**1d**; 0.40 mmol, 78.1 mg, 1.0 equiv.) according to General Procedure A. M.p. 98–100 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.82 (d, *J* = 16.1 Hz, 1 H), 7.22–7.14 (m, 2 H), 6.96 (dd, *J* = 7.4, 2.1 Hz, 1 H), 6.43 (d, *J* = 16.1 Hz, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.84 (s, 3 H), 3.18 (s, 3 H), 3.03 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.6, 153.8, 152.1, 139.5, 138.1, 128.7, 125.9, 120.0, 118.4, 113.4, 60.3, 56.0, 36.7, 36.5, 14.1 ppm. HRMS (MALDI): calcd. for $C_{15}H_{20}NO_5$ [M + H]$^+$ 294.1336; found 294.1331. IR: $\tilde{\nu}$ = 3088, 2984, 2940, 1721, 1635, 1582, 1482, 1280, 1185, 1158, 1028, 759, 751 cm$^{-1}$.

**Ethyl (*E*)-3-[3-Chloro-2-(dimethylcarbamoyloxy)phenyl]acrylate (3e):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as a colorless oil (95 mg, 80%) from 2-chlorophenyl dimethylcarbamate (**1e**; 0.40 mmol, 79.8 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.74 (d, *J* = 16.1 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.16 (t, *J* = 7.9 Hz, 1 H), 6.43 (d, *J* = 16.1 Hz, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 3.19 (s, 3 H), 3.03 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.4, 153.0, 146.4, 137.6, 131.3, 130.2, 128.7, 126.4, 125.6, 121.1, 60.5, 36.9, 36.5, 14.2 ppm. MS (EI): calcd. for $C_{14}H_{16}ClNO_4$ [$M^+$] 297.08; found 297.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-3,5-dimethylphenyl]acrylate (3f):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as a colorless oil (96.8 mg, 83%) from 2,4-dimethylphenyl dimethylcarbamate (**1f**; 0.40 mmol, 77.3 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.73 (d, *J* = 16.1 Hz, 1 H), 7.25 (br. s, 1 H), 7.03 (br. s, 1 H), 6.39 (d, *J* = 16.0 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 3.17 (s, 3 H), 3.01 (s, 3 H), 2.28 (s, 3 H), 2.14 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.8, 153.9, 146.6, 138.7, 135.0, 133.5, 131.3, 127.3, 125.1, 119.3, 60.2, 36.7, 36.3, 20.6, 15.9, 14.1 ppm. HRMS (MALDI): calcd. for $C_{16}H_{22}NO_4$ [M + H]$^+$ 292.1543; found 292.1538. IR: $\tilde{\nu}$ = 2929, 1716, 1636, 1473, 1387, 1275, 1203, 1158, 1037, 983, 863, 755 cm$^{-1}$.

**Ethyl (*E*)-3-[3,5-Di-*tert*-butyl-2-(dimethylcarbamoyloxy)phenyl]-acrylate (3g):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:15 to 1:5) as a colorless oil (90.3 mg, 60%) from 2,4-di-*tert*-butylphenyl dimethylcarbamate (**1g**; 0.40 mmol, 111.0 mg, 1.0 equiv.) according to General Pro-

cedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.64 (d, $J$ = 15.9 Hz, 1 H), 7.47 (d, $J$ = 2.3 Hz, 1 H), 7.44 (d, $J$ = 2.3 Hz, 1 H), 6.38 (d, $J$ = 15.9 Hz, 1 H), 4.23 (q, $J$ = 7.1 Hz, 2 H), 3.22 (s, 3 H), 3.03 (s, 3 H), 1.35 (s, 9 H), 1.31 (s, 9 H), 1.31 (t, $J$ = 7.1 Hz) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.8, 154.5, 147.6, 146.6, 141.6, 139.8, 128.3, 126.4, 122.1, 119.2, 60.2, 36.9, 36.4, 34.9, 34.6, 31.3, 30.5, 14.2 ppm. HRMS (MALDI): calcd. for $C_{22}H_{33}NO_4Na$ [M + Na]$^+$ 398.2302; found 398.2305. IR: $\tilde{\nu}$ = 2957, 1728, 1707, 1441, 1386, 1364, 1275, 1158, 1041, 981, 870, 751, 614 cm$^{-1}$.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-4-methylphenyl]acrylate (3h):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as a colorless oil (98.9 mg, 89%) from *m*-tolyl dimethylcarbamate (**1h**; 0.40 mmol, 71.7 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.80 (d, $J$ = 16.1 Hz, 1 H), 7.51 (d, $J$ = 8.0 Hz, 1 H), 7.03 (d, $J$ = 8.0 Hz, 1 H), 6.98 (s, 1 H), 6.39 (d, $J$ = 16.1 Hz, 1 H), 4.24 (q, $J$ = 7.1 Hz, 2 H), 3.17 (s, 3 H), 3.03 (s, 3 H), 2.36 (s, 3 H), 1.32 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.9, 154.2, 149.9, 141.7, 138.2, 126.9, 126.6, 124.3, 123.7, 118.5, 60.3, 36.7, 36.4, 21.2, 14.2 ppm. MS (EI): calcd. for $C_{15}H_{19}NO_4$ [M$^+$] 277.13; found 277.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-4-methoxyphenyl]acrylate (3i-a):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as a white solid (71.7 mg, 61%) from 3-methoxyphenyl dimethylcarbamate (**1i**; 0.40 mmol, 78.1 mg, 1.0 equiv.) according to General Procedure A. M.p. 70–71 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.75 (d, $J$ = 16.0 Hz, 1 H), 7.53 (d, $J$ = 8.8 Hz, 1 H), 6.76 (dd, $J$ = 8.8, 2.4 Hz, 1 H), 6.70 (d, $J$ = 2.5 Hz, 1 H), 6.30 (d, $J$ = 16.0 Hz, 1 H), 4.22 (q, $J$ = 7.1 Hz, 2 H), 3.79 (s, 3 H), 3.16 (s, 3 H), 3.01 (s, 3 H), 1.30 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.1, 161.8, 154.0, 151.3, 138.0, 128.1, 119.8, 117.0, 112.5, 108.3, 60.2, 55.5, 36.8, 36.4, 14.2 ppm. HRMS (MALDI): calcd. for $C_{15}H_{19}NO_5Na$ [M + Na]$^+$ 316.1155; found 316.1151. IR: $\tilde{\nu}$ = 2978, 2937, 2898, 1731, 1633, 1612, 1508, 1389, 1303, 1170, 980, 827, 804, 753 cm$^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-4-methoxy-1,3-phenylene]diacrylate (3i-b):**[11] The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as a yellow solid (45.5 mg, 29%) from **1i** (0.40 mmol, 78.1 mg, 1.0 equiv.) according to General Procedure A. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.71 (d, $J$ = 16.0 Hz, 1 H), 7.67 (d, $J$ = 15.5 Hz, 1 H), 7.59 (d, $J$ = 8.9 Hz, 1 H), 6.83 (d, $J$ = 8.9 Hz, 1 H), 6.72 (d, $J$ = 16.3 Hz, 1 H), 6.31 (d, $J$ = 16.0 Hz, 1 H), 4.23 (q, $J$ = 7.1 Hz, 2 H), 4.22 (q, $J$ = 7.1 Hz, 2 H), 3.91 (s, 3 H), 3.23 (s, 3 H), 3.01 (s, 3 H), 1.31 (t, $J$ = 7.1 Hz, 3 H), 1.30 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.4, 166.8, 160.9, 153.5, 150.0, 137.8, 134.3, 128.8, 123.1, 121.4, 118.1, 117.9, 108.9, 60.3, 55.9, 36.9, 36.5, 14.2 ppm. MS (EI): calcd. for $C_{20}H_{25}NO_7$ [M$^+$] 391.16; found 391.

**Ethyl (*E*)-3-[4-Chloro-2-(dimethylcarbamoyloxy)phenyl]acrylate (3j):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (90.6 mg, 76%) from 3-chlorophenyl dimethylcarbamate (**1j**; 0.40 mmol, 79.8 mg, 1.0 equiv.) according to General Procedure A for 36 h. M.p. 69–70 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.76 (d, $J$ = 16.1 Hz, 1 H), 7.54 (d, $J$ = 8.3 Hz, 1 H), 7.22–7.18 (m, 2 H), 6.41 (d, $J$ = 16.1 Hz, 1 H), 4.25 (q, $J$ = 7.1 Hz, 3 H), 3.16 (s, 3 H), 3.03 (s, 3 H), 1.33 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 153.6, 150.3, 137.1, 136.1, 127.9, 126.0, 125.9, 123.8, 120.1, 60.5, 36.8, 36.5, 14.2 ppm. HRMS (MALDI): calcd. for $C_{14}H_{16}ClNO_4Na$ [M + Na]$^+$ 320.0660; found 320.0655. IR: $\tilde{\nu}$ = 3085, 2988, 2941, 1724, 1708, 1631, 1596, 1382, 1308, 1207, 1161, 1082, 916, 836, 751, 459 cm$^{-1}$.

**Ethyl (*E*)-3-[4-Bromo-2-(dimethylcarbamoyloxy)phenyl]acrylate (3k):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (94.5 mg, 69%) from 3-bromophenyl dimethylcarbamate (**1k**; 0.40 mmol, 97.6 mg, 1.0 equiv.) according to General Procedure A for 48 h. M.p. 63–65 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.72 (d, $J$ = 16.1 Hz, 1 H), 7.44 (d, $J$ = 8.4 Hz, 1 H), 7.35 (d, $J$ = 1.8 Hz, 1 H), 7.32 (dd, $J$ = 8.4, 1.7 Hz, 1 H), 6.40 (d, $J$ = 16.1 Hz, 1 H), 4.22 (q, $J$ = 7.1 Hz, 2 H), 3.13 (s, 3 H), 3.00 (s, 3 H), 1.29 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 153.6, 150.2, 137.1, 128.8, 128.0, 126.6, 126.3, 123.9, 120.1, 60.5, 36.8, 36.4, 14.1 ppm. HRMS (MALDI): calcd. for $C_{14}H_{17}BrNO_4$ [M + H]$^+$ 342.0336; found 342.0334. IR: $\tilde{\nu}$ = 2986, 1734, 1716, 1637, 1591, 1482, 1386, 1319, 1217, 1185, 984, 890, 818, 748 cm$^{-1}$.

**Ethyl (*E*)-3-[3-(Dimethylcarbamoyloxy)naphthalen-2-yl]acrylate (3l):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (111.5 mg, 89%) from naphthalen-2-yl dimethylcarbamate (**1l**; 0.40 mmol, 86.1 mg, 1.0 equiv.) according to General Procedure A. M.p. 73–75 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.09 (s, 1 H), 7.94 (d, $J$ = 16.1 Hz, 1 H), 7.81 (d, $J$ = 7.8 Hz, 1 H), 7.75 (d, $J$ = 7.8 Hz, 1 H), 7.62 (s, 1 H), 7.49–7.42 (m, 2 H), 6.59 (d, $J$ = 16.0 Hz, 1 H), 4.28 (q, $J$ = 7.1 Hz, 2 H), 3.21 (s, 3 H), 3.05 (s, 3 H), 1.35 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.7, 154.4, 147.2, 138.8, 134.3, 130.9, 128.1, 127.9, 127.3, 127.2, 126.9, 126.0, 120.18, 120.16, 60.4, 36.8, 36.4, 14.2 ppm. HRMS (MALDI): calcd. for $C_{18}H_{19}NO_4Na$ [M + Na]$^+$ 336.1206; found 336.1209. IR: $\tilde{\nu}$ = 3056, 2988, 2944, 1740, 1715, 1639, 1624, 1387, 1314, 1241, 1173, 981, 881, 741, 667, 468 cm$^{-1}$.

**Methyl (*E*)-3-[1-(Dimethylcarbamoyloxy)naphthalen-2-yl]acrylate (3m):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:5) as an off-white solid (100.6 mg, 84%) from naphthalen-1-yl dimethylcarbamate (**1a**; 0.40 mmol, 86.1 mg, 1.0 equiv.) according to General Procedure A for 36 h. M.p. 99–101 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.99 (d, $J$ = 16.1 Hz, 1 H), 7.88–7.81 (m, 2 H), 7.73–7.66 (m, 2 H), 7.55–7.49 (m, 2 H), 6.55 (d, $J$ = 16.0 Hz, 1 H), 3.82 (s, 3 H), 3.35 (s, 3 H), 3.09 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.4, 154.3, 146.8, 138.4, 135.4, 128.03, 127.99, 127.5, 127.2, 126.2, 124.0, 122.9, 122.3, 119.5, 51.8, 37.1, 36.8 ppm. HRMS (MALDI): calcd. for $C_{17}H_{17}NO_4Na$ [M + Na]$^+$ 322.1050; found 322.1048. IR: $\tilde{\nu}$ = 3053, 2947, 1223, 1710, 1632, 1427, 1364, 1313, 1190, 1172, 1155, 985, 819, 760 cm$^{-1}$.

**Butyl (*E*)-3-[1-(Dimethylcarbamoyloxy)naphthalen-2-yl]acrylate (3n):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:4) as an off-white solid (114.8 mg, 84%) from **1a** (0.40 mmol, 86.1 mg, 1.0 equiv.) according to General Procedure A for 48 h. M.p. 61–62 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.99 (d, $J$ = 16.0 Hz, 1 H), 7.88–7.86 (m, 1 H), 7.82–7.80 (m, 1 H), 7.71–7.66 (m, 2 H), 7.54–7.49 (m, 2 H), 6.55 (d, $J$ = 16.0 Hz, 1 H), 4.23 (t, $J$ = 6.6 Hz, 2 H), 3.33 (s, 3 H), 3.08 (s, 3 H), 1.74–1.67 (m, 2 H), 1.51–1.42 (m, 2 H), 0.99 (t, $J$ = 7.4 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.8, 154.1, 146.6, 137.9, 135.1, 127.8, 127.3, 126.9, 126.0, 123.8, 122.6, 122.1, 119.7, 64.2, 36.8, 36.5, 30.6, 19.1, 13.6 (one signal missing due to overlap) ppm. HRMS (MALDI): calcd. for $C_{20}H_{23}NO_4Na$ [M + Na]$^+$ 364.1519; found 364.1514. IR: $\tilde{\nu}$ = 3060, 2963, 2868, 1727, 1630, 1362, 1297, 1249, 1174, 979, 806, 750, 663, 547 cm$^{-1}$.

**Benzyl (*E*)-3-[1-(Dimethylcarbamoyloxy)naphthalen-2-yl]acrylate (3o):** The title compound was isolated by column chromatography

(EtOAc/petroleum ether, 1:10 to 1:5) as an off-white solid (136.7 mg, 91%) from **1a** (0.40 mmol, 86.1 mg, 1.0 equiv.) according to General Procedure A. M.p. 87–89 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.04 (d, $J$ = 16.0 Hz, 1 H), 7.90–7.80 (m, 2 H), 7.73–7.67 (m, 2 H), 7.56–7.50 (m, 2 H), 7.46–7.36 (m, 5 H), 6.60 (d, $J$ = 16.0 Hz, 1 H), 5.28 (s, 2 H), 3.32 (s, 3 H), 3.07 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 154.2, 146.8, 138.6, 136.0, 135.3, 128.5, 128.1, 127.9, 127.4, 127.0, 126.1, 123.8, 122.7, 122.2, 119.3, 66.3, 36.9, 36.6 (two signals missing due to overlap) ppm. HRMS (MALDI): calcd. for $C_{23}H_{21}NO_4Na$ [M + Na]$^+$ 398.1363; found 398.1358. IR: $\tilde{\nu}$ = 3028, 2827, 1717, 1703, 1376, 1256, 1239, 1163, 1148, 1013, 820, 756, 701, 553 cm$^{-1}$.

**Compounds 3p:** According to the General Procedure A, **3p-a** (59.1 mg, 46% yield, off-white solid) and **3p-b** (53.8 mg, 32% yield, yellow solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from methyl 2-(dimethylcarbamoyloxy)benzoate (**1m**; 0.40 mmol, 89.3 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to the General Procedure A for 60 h, **3p-a** (41.1 mg, 32% yield, off-white solid) and **3p-b** (94.1 mg, 56% yield, yellow solid) were isolated.

**Methyl (*E*)-2-(Dimethylcarbamoyloxy)-3-(3-ethoxy-3-oxoprop-1-enyl)benzoate (3p-a):** M.p. 69–70 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.00 (dd, $J$ = 7.8, 1.5 Hz, 1 H), 7.87 (d, $J$ = 16.1 Hz, 1 H), 7.80 (dd, $J$ = 7.9, 1.3 Hz, 1 H), 7.30 (t, $J$ = 7.9 Hz, 1 H), 6.45 (d, $J$ = 16.1 Hz, 1 H), 4.26 (q, $J$ = 7.1 Hz, 2 H), 3.87 (s, 3 H), 3.20 (s, 3 H), 2.04 (s, 3 H), 1.33 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 164.8, 154.0, 149.7, 137.6, 133.1, 131.2, 129.5, 125.4, 124.7, 120.9, 60.6, 52.2, 36.8, 36.6, 14.2 ppm. HRMS (MALDI): calcd. for $C_{16}H_{20}NO_6$ [M + H]$^+$ 322.1285; found 322.1287. IR: $\tilde{\nu}$ = 2935, 1724, 1634,1437, 1385, 1322, 1301, 1264, 1160, 1136, 1090, 994, 848, 758 cm$^{-1}$. The structure of compound **3p-a** was further confirmed by HMBC and NOE experiments, see the Supporting Information (S6–S8) for details.

**Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-3-(methoxycarbonyl)-1,4-phenylene]diacrylate (3p-b):** M.p. 94–96 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.77–7.68 (m, 3 H), 7.49 (d, $J$ = 8.4 Hz, 1 H), 6.45 (d, $J$ = 16.1 Hz, 1 H), 6.38 (d, $J$ = 15.8 Hz, 1 H), 4.23 (q, $J$ = 7.1 Hz, 4 H), 3.90 (s, 3 H), 3.11 (s, 3 H), 3.00 (s, 3 H), 1.30 (t, $J$ = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.3, 166.0, 165.6, 153.4, 147.9, 140.4, 136.8, 135.9, 130.2, 128.7, 128.1, 124.1, 122.2, 121.4, 60.7, 60.6, 52.6, 36.9, 36.5, 14.2 (one signal missing due to overlap) ppm. HRMS (MALDI): calcd. for $C_{21}H_{26}NO_8$ [M + H]$^+$ 420.1653; found 420.1654. IR: $\tilde{\nu}$ = 2982, 1736, 1714, 1635, 1473, 1392, 1321, 1282, 1175, 1042, 980, 822, 750 cm$^{-1}$.

**Compounds 3q:** According to General Procedure A, **3q-a** (53.7 mg, 51%; off-white solid) and **3q-b** (63.7 mg, 44%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from phenyl dimethylcarbamate (**1n**; 0.40 mmol, 66.1 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, **3q-a** (29.6 mg, 28%; off-white solid) and **3q-b** (99.8 mg, 69%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from **1n** (0.40 mmol, 66.1 mg, 1.0 equiv.).

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)phenyl]acrylate (3q-a):**[11] $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.83 (d, $J$ = 16.1 Hz, 1 H), 7.60 (dd, $J$ = 7.8, 1.4 Hz, 1 H), 7.39–7.34 (m, 1 H), 7.20 (t, $J$ = 7.5 Hz, 1 H), 7.15 (dd, $J$ = 8.2, 0.8 Hz, 1 H), 6.43 (d, $J$ = 16.1 Hz, 1 H), 4.24 (q, $J$ = 7.1 Hz, 2 H), 3.16 (s, 3 H), 3.01 (s, 3 H), 1.31 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.7, 154.1, 150.0, 138.2, 130.9, 127.2, 127.1, 125.6, 123.3, 119.6, 60.4, 36.7, 36.4, 14.2 ppm. MS (EI): calcd. for $C_{14}H_{17}NO_4$ [M$^+$] 263.12; found 263.

**Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-1,3-phenylene]diacrylate (3q-b):**[11] $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.76 (d, $J$ = 16.1 Hz, 2 H), 7.66 (d, $J$ = 7.8 Hz, 2 H), 7.30–7.28 (m, 1 H), 6.45 (d, $J$ = 16.0 Hz, 2 H), 4.26 (q, $J$ = 7.1 Hz, 4 H), 3.27 (s, 3 H), 3.05 (s, 3 H), 1.34 (t, $J$ = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.4, 153.6, 148.6, 137.6, 129.1, 128.7, 126.1, 120.7, 60.5, 36.9, 36.5, 14.2 ppm. MS (EI): calcd. for $C_{19}H_{23}NO_6$ [M$^+$] 361.15; found 361.

**Compounds 3r:** According to General Procedure A, **3r-a** (72.7 mg, 61%; off-white solid) and **3r-b** (44.3 mg, 28%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from 4-chlorophenyl dimethylcarbamate (**1o**; 0.40 mmol, 79.8 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, **3r-a** (46.5 mg, 39%; off-white solid) and **3r-b** (95.1 mg, 60%; off-white solid) were isolated.

**Ethyl (*E*)-3-[5-Chloro-2-(dimethylcarbamoyloxy)phenyl]acrylate (3r-a):** M.p. 118–119 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.74 (d, $J$ = 16.1 Hz, 1 H), 7.58 (d, $J$ = 2.4 Hz, 1 H), 7.33 (dd, $J$ = 8.7, 2.5 Hz, 1 H), 7.12 (d, $J$ = 8.7 Hz, 1 H), 6.42 (d, $J$ = 16.1 Hz, 1 H), 4.26 (q, $J$ = 7.1 Hz, 2 H), 3.16 (s, 3 H), 3.03 (s, 3 H), 1.33 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.3, 153.8, 148.4, 136.9, 131.0, 130.6, 128.8, 126.8, 124.7, 120.9, 60.6, 36.8, 36.4, 14.2 ppm. HRMS (MALDI): calcd. for $C_{14}H_{16}ClNO_4Na$ [M + Na]$^+$ 320.0660; found 320.0658. IR: $\tilde{\nu}$ = 3088, 3065, 2984, 2934, 2906, 1732, 1704, 1481, 1388, 1285, 1221, 1181, 1166, 976, 871, 801, 754, 675, 459 cm$^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[5-Chloro-2-(dimethylcarbamoyloxy)-1,3-phenylene]diacrylate (3r-b):** M.p. 125–127 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.66 (d, $J$ = 16.0 Hz, 2 H), 7.59 (s, 2 H), 6.43 (d, $J$ = 16.0 Hz, 2 H), 4.25 (q, $J$ = 7.1 Hz, 4 H), 3.24 (s, 3 H), 3.03 (s, 3 H), 1.33 (t, $J$ = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.1, 153.4, 147.1, 136.5, 131.9, 130.8, 128.2, 122.0, 60.8, 37.1, 36.6, 14.2 ppm. HRMS (MALDI): calcd. for $C_{19}H_{22}ClNO_6Na$ [M + Na]$^+$ 418.1028; found 418.1026. IR: $\tilde{\nu}$ = 3082, 2990, 2904, 1717, 1637, 1388, 1318, 1259, 1184, 1154, 1035, 973, 751, 565 cm$^{-1}$.

**Compounds 3s:** According to General Procedure A, **3s-a** (82.1 mg, 60%; off-white solid) and **3s-b** (66.9 mg, 38%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from 4-bromophenyl dimethylcarbamate (**1p**; 0.40 mmol, 97.6 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, **3s-a** (43.8 mg, 32%; off-white solid) and **3s-b** (103.9 mg, 59%; off-white solid) were isolated.

**Ethyl (*E*)-3-[5-Bromo-2-(dimethylcarbamoyloxy)phenyl]acrylate (3s-a):** M.p. 102–104 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.76–7.71 (m, 2 H), 7.47 (dd, $J$ = 8.6, 2.2 Hz, 1 H), 7.07 (d, $J$ = 8.7 Hz, 1 H), 6.42 (d, $J$ = 16.1 Hz, 1 H), 4.26 (q, $J$ = 7.1 Hz, 2 H), 3.16 (s, 3 H), 3.02 (s, 3 H), 1.33 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.3, 153.7, 148.9, 136.7, 133.4, 129.8, 129.2, 125.0, 120.9, 118.6, 60.5, 36.8, 36.4, 14.1 ppm. HRMS (MALDI): calcd. for $C_{14}H_{17}BrNO_4$ [M + H]$^+$ 342.0336; found 342.0338. IR: $\tilde{\nu}$ = 3086, 2983, 2932, 1704, 1477, 1388, 1285, 1219, 1165, 1105, 975, 870, 753, 660, 455 cm$^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[5-Bromo-2-(dimethylcarbamoyloxy)-1,3-phenylene]diacrylate (3s-b):** M.p. 151–158 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.74 (s, 2 H), 7.65 (d, $J$ = 16.0 Hz, 2 H), 6.42 (d, $J$

= 16.0 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 4 H), 3.24 (s, 3 H), 3.03 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.1, 153.3, 147.6, 136.4, 131.21, 131.15, 122.0, 119.5, 60.8, 37.1, 36.6, 14.2 ppm. HRMS (MALDI): calcd. for $C_{19}H_{23}BrNO_6$ $[M + H]^+$ 440.0703; found 440.0706. IR: $\tilde{\nu}$ = 3078, 2988, 2902, 1720, 1638, 1317, 1258, 1183, 1152, 1036, 1003, 972, 860, 750 $cm^{-1}$.

**Compounds 3t:** According to General Procedure A, **3t-a** (58% yield) and **3t-b** (7% yield) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as an inseparable mixture (83.2 mg, off-white solid) from 4-nitrophenyl dimethylcarbamate (**1q**; 0.40 mmol, 84.1 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, **3t-a** (59% yield) and **3t-b** (16% yield) were isolated as an inseparable mixture (98.8 mg, off-white solid).

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-5-nitrophenyl]acrylate (3t-a) and Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-5-nitro-1,3-phenylene]diacrylate (3t-b):** $^1$H NMR ($CDCl_3$, 400 MHz) (mixture of **3t-a** and **3t-b**): $\delta$ = 8.50 (d, *J* = 2.6 Hz, 1 H, **3t-a**), 8.49 (br. s, 2 H, **3t-b**), 8.23 (dd, *J* = 9.0, 2.7 Hz, 1 H, **3t-a**), 7.82 (d, *J* = 16.1 Hz, 1 H, **3t-a**), 7.71 (d, *J* = 16.0 Hz, 2 H, **3t-b**), 7.41 (d, *J* = 9.0 Hz, 1 H, **3t-a**), 6.57 [d, *J* = 16.1 Hz, 1 H (**3t-a**) + 2 H (**3t-b**)], 4.28 [q, *J* = 7.1 Hz, 2 H (**3t-a**) + 4H (**3t-b**)], 3.27 (s, 3 H, **3t-b**), 3.19 (s, 3 H, **3t-a**), 3.05 [br. s, 3 H (**3t-a**) + 3 H (**3t-b**)], 1.35 [t, *J* = 7.1 Hz, 3 H (**3t-a**) + 3 H (**3t-b**)] ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz) (mixture of **3t-a** and **3t-b**): $\delta$ = 166.0, 154.3, 152.9, 152.6, 144.9, 136.0, 135.6, 130.9, 128.3, 125.4, 124.1, 123.5, 123.0, 122.6, 122.5, 61.0, 60.9, 37.1, 37.0, 36.7, 36.6, 14.2 ppm. HRMS (MALDI): calcd. for $C_{14}H_{16}N_2O_6Na$ (**3t-a**) $[M + Na]^+$ 331.0901; found 331.0905; calcd. for $C_{19}H_{22}N_2O_8Na$ (**3t-b**) $[M + Na]^+$ 429.1268; found 429.1271. IR: $\tilde{\nu}$ = 2925, 2360, 1733, 1716, 1687, 1519, 1508, 1387, 1346, 1283, 1256, 1159, 1045, 979, 877, 744, 667 $cm^{-1}$.

**Compounds 3u:** According to General Procedure A, **3u-a** (51.1 mg, 46%; off-white solid) and **3u-b** (78.1 mg, 52%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from *p*-tolyl dimethylcarbamate (**1r**; 0.40 mmol, 71.7 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, only **3u-b** (139.7 mg, 93%; off-white solid) was isolated.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-5-methylphenyl]acrylate (3u-a):** M.p. 88–89 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.80 (d, *J* = 16.0 Hz, 1 H), 7.41 (s, 1 H), 7.18 (d, *J* = 8.3 Hz, 1 H), 7.04 (d, *J* = 8.3 Hz, 1 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.16 (s, 3 H), 3.02 (s, 3 H), 2.34 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.6, 154.2, 147.8, 138.2, 135.0, 131.6, 127.3, 126.7, 122.9, 119.3, 60.2, 36.6, 36.2, 20.6, 14.1 ppm. HRMS (MALDI): calcd. for $C_{15}H_{20}NO_4$ $[M + H]^+$ 278.1387; found 278.1392. IR: $\tilde{\nu}$ = 3075, 3055, 2990, 2926, 1719, 1495, 1394, 1280, 1228, 1208, 1162, 1042, 997, 857, 811, 750, 559 $cm^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-5-methyl-1,3-phenylene]diacrylate (3u-b):** M.p. 121–122 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.70 (d, *J* = 16.0 Hz, 2 H), 7.44 (s, 2 H), 6.41 (d, *J* = 16.0 Hz, 2 H), 4.24 (q, *J* = 7.1 Hz, 4 H), 3.24 (s, 3 H), 3.02 (s, 3 H), 2.36 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 153.9, 146.6, 137.8, 135.7, 129.4, 128.6, 120.4, 60.4, 36.9, 36.5, 20.8, 14.2 ppm. HRMS (MALDI): calcd. for $C_{20}H_{25}NO_6Na$ $[M + Na]^+$ 398.1574; found 398.1570. IR: $\tilde{\nu}$ = 2989, 2934, 1716, 1637, 1457, 1389, 1321, 1266, 1182, 1043, 975, 857, 753, 568 $cm^{-1}$.

**Compounds 3v:** According to General Procedure A, **3v-a** (57.5 mg, 49%; off-white solid) and **3v-b** (70.6 mg, 45%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from 4-methoxyphenyl dimethylcarbamate (**1s**; 0.40 mmol, 78.1 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, only **3v-b** (131.6 mg, 84%; off-white solid) was isolated.

**Ethyl (*E*)-3-[2-(Dimethylcarbamoyloxy)-5-methoxyphenyl]acrylate (3v-a):** M.p. 96–98 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.78 (d, *J* = 16.1 Hz, 1 H), 7.09–7.06 (m, 2 H), 6.93 (dd, *J* = 9.0, 3.0 Hz, 1 H), 6.41 (d, *J* = 16.1 Hz, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 3.82 (s, 3 H), 3.16 (s, 3 H), 3.02 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.6, 156.8, 154.6, 143.8, 138.2, 127.8, 124.2, 119.8, 117.0, 111.0, 60.4, 55.5, 36.7, 36.4, 14.2 ppm. HRMS (MALDI): calcd. for $C_{15}H_{19}NO_5Na$ $[M + Na]^+$ 316.1155; found 316.1149. IR: $\tilde{\nu}$ = 2930, 1718, 1637, 1490, 1387, 1275, 1242, 1203, 1158, 1037, 983, 863, 755 $cm^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[2-(Dimethylcarbamoyloxy)-5-methoxy-1,3-phenylene]diacrylate (3v-b):** M.p. 126–128 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.70 (d, *J* = 16.0 Hz, 2 H), 7.15 (s, 2 H), 6.41 (d, *J* = 16.0 Hz, 2 H), 4.25 (q, *J* = 7.1 Hz, 4 H), 3.84 (s, 3 H), 3.24 (s, 3 H), 3.03 (s, 3 H), 1.33 (t, *J* = 7.1 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.4, 156.9, 154.1, 142.7, 137.7, 129.7, 120.8, 113.8, 60.6, 55.6, 36.9, 36.5, 14.2 ppm. HRMS (MALDI): calcd. for $C_{20}H_{25}NO_7Na$ $[M + Na]^+$ 414.1523; found 414.1516. IR: $\tilde{\nu}$ = 2984, 2930, 1735, 1709, 1638, 1462, 1391, 1341, 1265, 1182, 1158, 984, 856, 756, 577 $cm^{-1}$.

**Compounds 3w:** According to General Procedure A, **3w-a** (62.7 mg, 49%; off-white solid) and **3w-b** (71.7 mg, 43%; off-white solid) were isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) from 4-*tert*-butylphenyl dimethylcarbamate (**1t**; 0.40 mmol, 88.5 mg, 1.0 equiv.). By using $[RuCl_2(p\text{-cymene})]_2$ (10.0 mol-%), $AgSbF_6$ (40 mol-%), $Cu(OAc)_2$ (4.0 equiv.), and acrylates (5.0 equiv.), according to General Procedure A for 60 h, only **3w-b** (143.8 mg, 86%; off-white solid) was isolated.

**Ethyl (*E*)-3-[5-*tert*-Butyl-2-(dimethylcarbamoyloxy)phenyl]acrylate (3w-a):** M.p. 138–140 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.83 (d, *J* = 16.1 Hz, 1 H), 7.59 (s, 1 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 7.08 (d, *J* = 8.6 Hz, 1 H), 6.44 (d, *J* = 16.1 Hz, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.15 (s, 3 H), 3.01 (s, 3 H), 1.32 (t, *J* = 7.3 Hz, 3 H), 1.31 (s, 9 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.8, 154.3, 148.3, 147.8, 138.9, 128.3, 126.3, 123.9, 122.7, 119.2, 60.3, 36.7, 36.3, 34.4, 31.2, 14.2 ppm. HRMS (MALDI): calcd. for $C_{18}H_{26}NO_4$ $[M + H]^+$ 320.1856; found 320.1856. IR: $\tilde{\nu}$ = 3080, 2985, 2958, 2901, 2868, 1727, 1707, 1637, 1493, 1390, 1364, 1325, 1222, 1162, 1035, 990, 858, 751 $cm^{-1}$.

**Diethyl (2*E*,2′*E*)-3,3′-[5-*tert*-Butyl-2-(dimethylcarbamoyloxy)-1,3-phenylene]diacrylate (3w-b):** M.p. 115–117 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.72 (d, *J* = 16.1 Hz, 2 H), 7.63 (s, 2 H), 6.42 (d, *J* = 16.0 Hz, 2 H), 4.23 (q, *J* = 7.1 Hz, 4 H), 3.22 (s, 3 H), 3.01 (s, 3 H), 1.32 (s, 9 H), 1.31 (t, *J* = 7.3 Hz, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 166.5, 153.8., 148.7, 146.5, 138.3, 128.2, 126.1, 120.3, 60.4, 36.9, 36.4, 34.5, 31.1, 14.2 ppm. HRMS (MALDI): calcd. for $C_{23}H_{31}NO_6Na$ $[M + Na]^+$ 440.2044; found 440.2047. IR: $\tilde{\nu}$ = 3066, 2959, 1731, 1714, 1699, 1639, 1387, 1368, 1278, 1243, 1181, 1161, 1041, 991, 880, 753, 702, 581 $cm^{-1}$.

**2-[(*E*)-2-(Phenylsulfonyl)vinyl]naphthalen-1-yl Dimethylcarbamate (3-Sulfone):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:1, then MeOH/$CH_2Cl_2$, 1:1) as a brown solid (65.1 mg, 43%) from **1a** (0.40 mmol,

86 mg, 1.0 equiv.) according to General Procedure A for 24 h. M.p. 205–206 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.98–7.95 (m, 3 H), 7.89–7.86 (m, 1 H), 7.83–7.81 (m, 1 H), 7.69 (d, $J$ = 8.7 Hz, 1 H), 7.63–7.61 (m, 1 H), 7.58–7.54 (m, 4 H), 7.53 (d, $J$ = 5.7 Hz, 1 H), 6.93 (d, $J$ = 15.5 Hz, 1 H), 3.36 (s, 3 H), 3.10 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.0, 147.5, 140.5, 136.4, 135.6, 133.4, 129.7, 129.3, 128.6, 128.0, 127.9, 127.8, 127.3, 126.4, 122.8, 122.4, 122.1, 37.1, 36.8 ppm. HRMS (MALDI): calcd. for $C_{21}H_{19}NNaO_4S$ [M + Na]$^+$ 404.0927; found 404.0926. IR: $\tilde{\nu}$ = 3054, 2962, 2926, 1722, 1616, 1450, 1364, 1304, 1262, 1146, 1086, 846, 740, 610, 559 cm$^{-1}$.

**Ethyl (*E*)-3-[1-(Dimethylcarbamoyloxy)-3,4-dihydronaphthalen-2-yl-]acrylate (3x):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as a yellow solid (42.5 mg, 45%) from 3,4-dihydronaphthalen-1-yl dimethylcarbamate (**1u**; 0.30 mmol, 65.1 mg, 1.0 equiv.) according to General Procedure A for 40 h, but $[RuCl_2(p\text{-cymene})]_2$ (7.5 mol-%), $AgSbF_6$ (30 mol-%), and AgOAc (3.0 equiv.) were used. M.p. 102–103 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.77 (d, $J$ = 15.8 Hz, 1 H), 7.22–7.15 (m, 4 H), 6.01 (d, $J$ = 15.8 Hz, 1 H), 4.23 (q, $J$ = 7.1 Hz, 2 H), 3.23 (s, 3 H), 3.02 (s, 3 H), 2.94 (t, $J$ = 7.9 Hz, 2 H), 2.60 (t, $J$ = 7.9 Hz, 2 H), 1.31 (t, $J$ = 7.1 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.3, 153.9, 147.9, 138.5, 137.4, 130.9, 128.9, 127.5, 126.7, 122.4, 122.3, 118.0, 60.3, 36.9, 36.6, 27.2, 22.8, 14.3 ppm. HRMS (MALDI): calcd. for $C_{18}H_{21}NO_4Na$ [M + Na]$^+$ 338.1363; found 338.1366. IR: $\tilde{\nu}$ = 3066, 2976, 2951, 2891, 1732, 1614, 1392, 1314, 1171, 1230, 1029, 973, 858, 771 cm$^{-1}$.

**Butyl (*E*)-3-[1-(Dimethylcarbamoyloxy)-3,4-dihydronaphthalen-2-yl-]acrylate (3y):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as a yellow oil (40.2 mg, 39%) from **1u** (0.30 mmol, 65.1 mg, 1.0 equiv.) according to General Procedure A for 40 h, but $[RuCl_2(p\text{-cymene})]_2$ (7.5 mol-%), $AgSbF_6$ (30 mol-%), and AgOAc (3.0 equiv.) were used. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.76 (d, $J$ = 15.8 Hz, 1 H), 7.22–7.16 (m, 4 H), 6.01 (d, $J$ = 15.8 Hz, 1 H), 4.17 (t, $J$ = 6.6 Hz, 2 H), 3.23 (s, 3 H), 3.02 (s, 3 H), 2.93 (t, $J$ = 8.0 Hz, 2 H), 2.60 (t, $J$ = 8.0 Hz, 2 H), 1.71–1.62 (m, 3 H), 1.49–1.36 (m, 3 H), 0.96 (t, $J$ = 7.3 Hz, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.3, 153.8, 147.9, 138.4, 137.3, 130.8, 128.9, 127.4, 126.6, 122.34, 122.25, 118.0, 64.2, 36.8, 36.5, 30.7, 27.1, 22.7, 19.1, 13.7 ppm. HRMS (MALDI): calcd. for $C_{20}H_{25}NO_4Na$ [M + Na]$^+$ 366.1676; found 366.1672. IR: $\tilde{\nu}$ = 2957, 1732, 1615, 1507, 1457, 1394, 1313, 1245, 1168, 1078, 764 cm$^{-1}$.

**Butyl (*E*)-3-[1-(Dimethylcarbamoyloxy)-3,4-dihydronaphthalen-2-yl-]acrylate (3z):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:10 to 1:5) as a yellow oil (66.9 mg, 59%) from **1u** (0.30 mmol, 65.1 mg, 1.0 equiv.) according to General Procedure A for 40 h, but $[RuCl_2(p\text{-cymene})]_2$ (7.5 mol-%), $AgSbF_6$ (30 mol-%), and AgOAc (3.0 equiv.) were used. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.88 (d, $J$ = 15.8 Hz, 1 H), 7.45–7.38 (m, 6 H), 7.31–7.22 (m, 3 H), 6.13 (d, $J$ = 15.8 Hz, 1 H), 5.28 (s, 2 H), 3.26 (s, 3 H), 3.06 (s, 3 H), 2.99 (t, $J$ = 8.0 Hz, 2 H), 2.65 (t, $J$ = 7.9 Hz, 2 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 167.0, 153.8, 148.1, 139.1, 137.4, 136.1, 130.8, 129.0, 128.5, 128.1, 127.4, 126.6, 122.30, 122.28, 117.5, 66.1, 36.8, 36.5, 27.1, 22.6 ppm. HRMS (MALDI): calcd. for $C_{23}H_{23}NO_4Na$ [M + Na]$^+$ 400.1519; found 400.1525. IR: $\tilde{\nu}$ = 3031, 2940, 1727, 1613, 1454, 1393, 1310, 1246, 1160, 1077, 981, 757, 698 cm$^{-1}$.

**General Procedure for the Rh$^{III}$-Catalyzed Alkyne Hydroarylation of Phenol Carbamate Derivatives (General Procedure B):** A mixture of $[Cp^*RhCl_2]_2$ (9.18 mg, 0.015 mmol, 5.0 mol-%), $AgSbF_6$ (20.7 mg, 0.06 mmol, 20.0 mol-%), phenyl carbamate (**1**; 0.3 mmol), PivOH (245 mg, 2.4 mmol), and alkyne (0.6 mmol) was combined in a Schlenk tube with a stir bar, then PhCl (2.0 mL) was added under Ar. The reaction mixture was heated to the desired temperature with stirring for the desired reaction time, then the vial was cooled to room temp., and the crude product was purified by flash chromatography on silica gel.

**(*E*)-2-(1,2-Diphenylvinyl)naphthalen-1-yl Dimethylcarbamate (5a):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as a yellow solid (116.9 mg, 99%) from **1a** (0.30 mmol, 64.6 mg, 1.0 equiv.) according to General Procedure B for 18 h. M.p. 101–102 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.94–7.91 (m, 1 H), 7.85 (dd, $J$ = 6.3, 2.9 Hz, 1 H), 7.69 (d, $J$ = 8.5 Hz, 1 H), 7.55–7.47 (m, 2 H), 7.35 (d, $J$ = 8.5 Hz, 1 H), 7.28–7.24 (m, 5 H), 7.20–7.12 (m, 5 H), 6.92 (s, 1 H), 2.86 (s, 3 H), 2.84 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.1, 144.5, 140.1, 138.9, 137.3, 133.9, 133.2, 131.5, 130.2, 129.4, 128.20, 128.17, 128.1, 127.9, 127.7, 127.2, 126.8, 126.5, 126.2, 125.2, 121.9, 36.6, 36.2 ppm. HRMS (MALDI): calcd. for $C_{27}H_{23}NO_2Na$ [M + Na]$^+$ 416.1621; found 416.1623. IR: $\tilde{\nu}$ = 3055, 3019, 2925, 1719, 1599, 1490, 1445, 1343, 1146, 1083, 820, 751, 670 cm$^{-1}$.

**(*E*)-2-(1,2-Diphenylvinyl)-6-methoxyphenyl Dimethylcarbamate (5b):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20 to 1:10) as a colorless oil (69.5 mg, 62%) from 2-methoxyphenyl dimethylcarbamate (**1d**; 0.30 mmol, 58.6 mg, 1.0 equiv.) according to General Procedure B for 30 h. M.p. 145–147 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.30 (br. s, 5 H), 7.23–7.16 (m, 6 H), 7.03–6.99 (m, 2 H), 6.87 (s, 1 H), 3.92 (s, 3 H), 2.86 (s, 3 H), 2.77 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.6, 152.3, 139.9, 138.8, 138.5, 138.2, 137.2, 130.9, 129.8, 129.4, 128.0, 127.8, 126.9, 126.7, 125.5, 122.6, 111.5, 56.1, 36.5, 36.1 ppm. HRMS (MALDI): calcd. for $C_{24}H_{24}NO_3$ [M + H]$^+$ 374.1751; found 374.1745. IR: $\tilde{\nu}$ = 3021, 2936, 1725, 1576, 1468, 1441, 1387, 1271, 1204, 1164, 1080, 779, 754, 697 cm$^{-1}$.

**(*E*)-2-[2-Chloro-6-(1,2-diphenylvinyl)phenyl]-*N*,*N*-dimethylacetamide (5c):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as an off-white solid (72.6 mg, 64%) from 2-chlorophenyl dimethylcarbamate (**1e**; 0.30 mmol, 59.9 mg, 1.0 equiv.) according to General Procedure B for 30 h. M.p. 177–179 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.38 (dd, $J$ = 7.9, 1.6 Hz, 1 H), 7.24–7.17 (m, 6 H), 7.16–7.12 (m, 4 H), 7.08–7.06 (m, 2 H), 6.78 (s, 1 H), 2.79 (s, 3 H), 2.69 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 152.7, 145.4, 139.61, 139.59, 138.3, 136.9, 131.5, 129.9, 129.4, 129.2, 128.5, 128.1, 127.9, 127.2, 127.0, 126.0, 36.6, 36.1 (one signal missing due to overlap) ppm. HRMS (MALDI): calcd. for $C_{23}H_{20}ClNO_2Na$ [M + Na]$^+$ 400.1075; found 400.1073. IR: $\tilde{\nu}$ = 3020, 2924, 1736, 1638, 1617, 1438, 1379, 1222, 1157, 780, 705, 691, 601 cm$^{-1}$.

**(*E*)-2-(1,2-Diphenylvinyl)-4,6-dimethylphenyl Dimethylcarbamate (5d):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as an off-white solid (75.8 mg, 68%) from 2,4-dimethylphenyl dimethylcarbamate (**1f**; 0.30 mmol, 58.0 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 142–144 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.22 (br. s, 5 H), 7.16–7.12 (m, 3 H), 7.10–7.08 (m, 2 H), 7.01 (s, 1 H), 6.96 (s, 1 H), 6.76 (s, 1 H), 2.77 (s, 3 H), 2.67 (s, 3 H), 2.30 (s, 3 H), 2.17 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.7, 145.3, 140.1, 139.4, 137.4, 137.1, 134.6, 131.2, 131.0, 130.5, 129.9, 129.4, 129.3, 127.9, 127.8, 126.9, 126.6, 36.4, 36.0, 20.7, 16.3 ppm. HRMS (MALDI): calcd. for $C_{25}H_{25}NO_2Na$ [M + Na]$^+$ 394.1778; found 394.1776. IR: $\tilde{\nu}$ = 3044, 2954, 2925, 1724, 1712, 1493, 1444, 1383, 1205, 1169, 1141, 860, 698 cm$^{-1}$.

**(*E*)-2,4-Di-*tert*-Butyl-6-(1,2-diphenylvinyl)phenyl Dimethylcarbamate (5e):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as an off-white solid (101.1 mg, 74%) from 2,4-di-*tert*-butylphenyl dimethylcarbamate (**1g**; 0.30 mmol, 78.7 mg, 1.0 equiv.) according to General Procedure B for 18 h. M.p. 122–124 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.35 (d, $J$ = 2.4 Hz, 1 H), 7.25–7.21 (m, 2 H), 7.20–7.15 (m, 4 H), 7.12–7.10 (m, 4 H), 7.05 (d, $J$ = 2.4 Hz, 1 H), 6.78 (s, 1 H), 2.80 (s, 3 H), 2.58 (s, 3 H), 1.36 (s, 9 H), 1.26 (s, 9 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 154.1, 146.8, 145.5, 141.1, 140.3, 139.9, 137.82, 137.79, 130.4, 130.3, 129.3, 127.84, 127.79, 127.0, 126.6, 126.4, 123.4, 36.6, 35.8, 34.9, 34.5, 31.4, 30.6 ppm. HRMS (MALDI): calcd. for $C_{31}H_{37}NO_2Na$ [M + Na]$^+$ 478.2717; found 478.2714. IR: $\tilde{\nu}$ = 3045, 3019, 2863, 1723, 1437, 1386, 1360, 1221, 1205, 1167, 1146, 779, 750, 694 cm$^{-1}$.

**(*E*)-5-Chloro-2-(1,2-diphenylvinyl)phenyl Dimethylcarbamate (5f):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as a yellow solid (85.1 mg, 75%) from 3-chlorophenyl dimethylcarbamate (**1j**; 0.30 mmol, 59.9 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 79–80 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.34–7.28 (m, 5 H), 7.27–7.25 (m, 1 H), 7.24 (d, $J$ = 1.9 Hz, 1 H), 7.23–7.21 (m, 3 H), 7.19 (d, $J$ = 2.0 Hz, 1 H), 7.16–7.14 (m, 2 H), 6.83 (s, 1 H), 2.82 (s, 3 H), 2.66 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.6, 149.4, 139.5, 138.1, 137.0, 135.8, 133.5, 131.9, 131.1, 129.9, 129.4, 128.1, 128.0, 127.3, 127.0, 125.7, 123.9, 36.5, 36.0 ppm. HRMS (MALDI): calcd. for $C_{23}H_{20}ClNO_2Na$ [M + Na]$^+$ 400.1075; found 400.1070. IR: $\tilde{\nu}$ = 2925, 1733, 1684, 1653, 1473, 1490, 1386, 1206, 1155, 775, 703, 693, 487 cm$^{-1}$.

**(*E*)-5-Bromo-2-(1,2-diphenylvinyl)phenyl Dimethylcarbamate (5g):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as an off-white solid (79.8 mg, 63%) from 3-bromophenyl dimethylcarbamate (**1k**; 0.30 mmol, 73.2 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 109–111 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.34 (dd, $J$ = 8.2, 1.8 Hz, 1 H), 7.28 (d, $J$ = 1.7 Hz, 1 H), 7.24–7.14 (m, 9 H), 7.10–7.08 (m, 2 H), 6.77 (s, 1 H), 2.76 (s, 3 H), 2.60 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.6, 149.5, 139.4, 138.1, 136.9, 136.2, 132.1, 131.1, 129.8, 129.4, 128.5, 128.1, 127.9, 127.3, 127.0, 126.7, 121.2, 36.4, 36.0 ppm. HRMS (MALDI): calcd. for $C_{23}H_{20}BrNO_2Na$ [M + Na]$^+$ 444.0570; found 444.0573. IR: $\tilde{\nu}$ = 3059, 2926, 1727, 1652, 1489, 1388, 1203, 1156, 775, 744, 702, 692 cm$^{-1}$.

**(*E*)-2-[1,2-Bis(4-chlorophenyl)vinyl]naphthalen-1-yl Dimethylcarbamate (5h):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as a yellow solid (59.6 mg, 86%) from naphthalen-1-yl dimethylcarbamate (**1a**; 0.15 mmol, 32.3 mg, 1.0 equiv.) according to General Procedure B for 30 h. M.p. 199–201 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.90–7.87 (m, 1 H), 7.83–7.80 (m, 1 H), 7.65 (d, $J$ = 8.5 Hz, 1 H), 7.52–7.46 (m, 2 H), 7.23–7.13 (m, 7 H), 7.01 (d, $J$ = 8.5 Hz, 2 H), 6.82 (s, 1 H), 2.82 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.9, 144.6, 138.5, 138.1, 135.5, 134.0, 133.3, 132.7, 132.3, 131.6, 130.6, 128.5, 128.3, 128.1, 127.8, 127.7, 126.7, 126.5, 125.4, 121.9, 36.6, 36.2 (one signal missing due to overlap) ppm. HRMS (MALDI): calcd. for $C_{27}H_{21}Cl_2NO_2Na$ [M + Na]$^+$ 484.0841; found 484.0844. IR: $\tilde{\nu}$ = 3057, 2925, 1723, 1489, 1356, 1151, 1092, 1081, 1012, 814, 750 cm$^{-1}$.

**(*E*)-2-[1,2-Bis(4-bromophenyl)vinyl]naphthalen-1-yl Dimethylcarbamate (5i):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20) as a yellow solid (79.4 mg, 96%) from **1a** (0.15 mmol, 32.3 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 168–169 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.91–7.88 (m, 1 H), 7.85–7.82 (m, 1 H), 7.67 (d, $J$ = 8.5 Hz, 1 H), 7.54–7.49 (m, 2 H), 7.37 (d, $J$ = 8.5 Hz, 2 H), 7.32 (d, $J$ = 8.5 Hz, 2 H), 7.28–7.25 (m, 1 H), 7.12 (d, $J$ = 8.4 Hz, 2 H), 6.97 (d, $J$ = 8.4 Hz, 2 H), 6.82 (s, 1 H), 2.84 (s, 6 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 153.9, 144.6, 138.63, 138.60, 135.9, 134.1, 132.3, 132.0, 131.5, 131.3, 130.9, 130.6, 128.1, 127.8, 127.7, 126.7, 126.5, 125.4, 121.9, 121.6, 121.0, 36.7, 36.2 ppm. HRMS (MALDI): calcd. for $C_{27}H_{21}Br_2NO_2Na$ [M + Na]$^+$ 571.9831; found 571.9830. IR: $\tilde{\nu}$ = 3054, 2925, 1723, 1486, 1354, 1150, 1161, 1070, 1009, 813, 748, 493 cm$^{-1}$.

**(*E*)-3-(1,2-Diphenylvinyl)-2-oxo-2*H*-chromen-4-yl Dimethylcarbamate (5j):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20 to 1:3) as a yellow solid (113.5 mg, 92%) from 2-oxo-2*H*-chromen-4-yl dimethylcarbamate (**1v**; 0.30 mmol, 69.9 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 223–225 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.70–7.62 (m, 2 H), 7.48–7.41 (m, 4 H), 7.38–7.33 (m, 4 H), 7.28–7.26 (m, 2 H), 7.23–7.20 (m, 2 H), 6.97 (s, 1 H), 2.99 (s, 3 H), 2.96 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.0, 156.1, 152.4, 152.0, 137.9, 136.0, 133.6, 132.0, 131.7, 129.4, 129.3, 128.1, 127.9, 127.4, 127.3, 124.2, 123.5, 121.8, 117.1, 116.4, 36.7, 36.4 ppm. HRMS (MALDI): calcd. for $C_{26}H_{21}NO_4Na$ [M + Na]$^+$ 434.1363; found 434.1361. IR: $\tilde{\nu}$ = 3022, 2930, 1725, 1605, 1489, 1443, 1339, 1144, 1047, 963, 764, 708, 693, 524 cm$^{-1}$.

**(*E*)-2-Oxo-3-(1-phenylprop-1-en-2-yl)-2*H*-chromen-4-yl Dimethylcarbamate (5k):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20 to 1:3) as an off-white solid (93.3 mg, 89%) from **1v** (0.30 mmol, 69.9 mg, 1.0 equiv.) according to General Procedure B for 24 h. M.p. 127–129 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.64 (d, $J$ = 7.8 Hz, 1 H), 7.54 (t, $J$ = 7.7 Hz, 1 H), 7.39–7.28 (m, 7 H), 6.55 (s, 1 H), 3.04 (s, 3 H), 2.95 (s, 3 H), 2.20 (s, 3 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.2, 154.8, 152.3, 152.0, 136.7, 131.9, 131.8, 129.6, 128.8, 128.1, 127.0, 124.2, 123.3, 122.4, 117.0, 116.5, 36.9, 36.6, 16.7 ppm. HRMS (MALDI): calcd. for $C_{21}H_{19}NO_4Na$ [M + Na]$^+$ 372.1206; found 372.1209. IR: $\tilde{\nu}$ = 2924, 1747, 1734, 1716, 1541, 1489, 1457, 1339, 1141, 1110, 1018, 766, 696, 668 cm$^{-1}$.

**(*E*)-2-Oxo-3-(1-phenylbut-1-en-2-yl)-2*H*-chromen-4-yl Dimethylcarbamate (5l):** The title compound was isolated by column chromatography (EtOAc/petroleum ether, 1:20 to 1:3) as a yellow oil (99.2 mg, 91%) from **1v** (0.30 mmol, 69.9 mg, 1.0 equiv.) according to General Procedure B for 24 h. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.45–7.42 (m, 2 H), 7.28 (br. s, 1 H), 7.24 (br. s, 1 H), 7.22–7.14 (m, 5 H), 6.48 (s, 1 H), 2.99 (s, 3 H), 2.87 (s, 3 H), 2.58 (q, $J$ = 7.4 Hz, 3 H), 0.94 (t, $J$ = 7.6 Hz, 4 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.3, 156.0, 152.7, 152.4, 136.7, 134.9, 131.8, 131.6, 128.6, 128.2, 127.9, 127.0, 124.2, 123.5, 122.0, 117.1, 116.5, 36.8, 36.6, 23.4, 12.9 ppm. HRMS (MALDI): calcd. for $C_{22}H_{21}NO_4Na$ [M + Na]$^+$ 386.1363; found 386.1362. IR: $\tilde{\nu}$ = 3055, 3023, 2967, 2934, 2876, 1733, 1608, 1489, 1456, 1338, 1267, 1148, 1093, 1048, 752, 702, 592 cm$^{-1}$.

**Deprotection of Carbamate 3a; (*E*)-3-(1-Hydroxynaphthalen-2-yl)-acrylic Acid (6):**[35] NaOH (200 mg, 5 mmol) was added to a solution of carbamate **3a** (156.5 mg, 0.5 mmol) in EtOH (5 mL), and the reaction mixture was stirred at 80 °C for 16 h. EtOH was evaporated, the residue was diluted with $Et_2O$ (20 mL), and the excess of NaOH was neutralized at 0 °C by using a solution of 3 M HCl. The aqueous solution was extracted with $Et_2O$ (3× 20 mL), and the combined organic layers were washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The crude product was washed with $CH_2Cl_2$ to afford **6** (92 mg, 86%) as a

yellow solid. $^1$H NMR ([D$_6$]DMSO, 400 MHz): $\delta$ = 12.27 (s, 1 H), 10.21 (s, 1 H), 8.30 (d, $J$ = 9.0 Hz, 1 H), 8.22 (d, $J$ = 16.0 Hz, 1 H), 7.86–7.84 (m, 1 H), 7.74 (d, $J$ = 8.7 Hz, 1 H), 7.56–7.50 (m, 2 H), 7.42 (d, $J$ = 8.7 Hz, 1 H), 6.51 (d, $J$ = 15.9 Hz, 1 H) ppm. $^{13}$C NMR ([D$_6$]DMSO, 100 MHz): $\delta$ = 168.2, 152.5, 139.2, 135.2, 127.8, 127.5, 125.7, 125.6, 124.0, 123.0, 120.2, 117.5, 116.4 ppm. MS (EI): calcd. for $C_{13}H_{10}O_3$ [M$^+$] 214.06; found 214.

**Deprotection of Carbamate 5a; 2-[(*E*)-1,2-Diphenylvinyl]naphthalen-1-ol (7):** NaOH (400mg, 10.0 mmol) was added to a solution of carbamate **5a** (196.6 mg, 0.5 mmol) in EtOH (5 mL), and the reaction mixture was stirred at 80 °C for 25 h. EtOH was evaporated, the residue was diluted with $Et_2O$ (20 mL), and the excess of NaOH was neutralized at 0 °C by using a solution of 3 M HCl. The aqueous solution was extracted with $Et_2O$ (3× 20 mL), and the combined organic layers were washed with brine, dried with $Na_2SO_4$, and concentrated under reduced pressure. The crude product was washed with EtOAc/petroleum ether (1:20) to afford **7** (145 mg, 90%) as a yellow liquid. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.31 (d, $J$ = 8.1 Hz, 1 H), 7.94 (d, $J$ = 7.7 Hz, 1 H), 7.66–7.56 (m, 4 H), 7.51–7.46 (m, 3 H), 7.45–7.43 (m, 2 H), 7.38 (d, $J$ = 9.8 Hz, 2 H), 7.29 (d, $J$ = 8.4 Hz, 1 H), 7.24–7.25 (m, 3 H), 5.77 (s, 1 H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 148.3, 141.7, 136.7, 136.2, 134.5, 130.9, 129.0, 128.6, 128.5, 128.3, 128.2, 128.0, 127.5, 127.3, 126.6, 125.3, 124.4, 122.8, 120.7, 119.0 ppm. HRMS (MALDI): calcd. for $C_{24}H_{19}O$ [M + H]$^+$ 323.1430; found 323.1430. IR: $\tilde{\nu}$ = 3517, 3055, 3022, 1598, 1571, 1492, 1447, 1389, 1263, 1080, 878, 764, 694, 567 cm$^{-1}$.

**X-ray Crystallography:** Data collection was performed with a Rigaku Saturn 70 diffractometer equipped with a rotating anode system by using graphite-monochromated Mo-$K_\alpha$ radiation ($\omega$-2$\theta$ scans). Semiempirical absorption corrections were applied for all complexes.[36] The structures were solved by direct methods and refined by full-matrix least squares. All calculations were carried out by using the SHELXL-97 program system.[37] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure-factor calculations. The crystal data and summary of the X-ray data collection are presented in Table S3. CCDC-911370 (**5a**) and 911369 (**5k**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see footnote on the first page of this article): Detailed procedures of remaining experiments, crystal data of compounds **5a** and **5k**, and full spectroscopic data for all new compounds.

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