JOC The Journal of Organic Chemistry

Article

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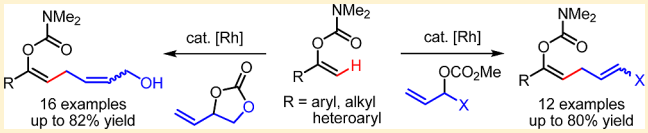
Mild and Site-Selective Allylation of Enol Carbamates with Allylic Carbonates under Rhodium Catalysis

Satyasheel Sharma, Sang Hoon Han, Yongguk Oh, Neeraj Kumar Mishra, Sangil Han, Jong Hwan Kwak, Seok-Yong Lee, Young Hoon Jung, and In Su Kim*

School of Pharmacy, Sungkyunkwan University, Suwon 440-746, Republic of Korea

Supporting Information

ABSTRACT: The rhodium(III)-catalyzed mild and site-selective C−H allylation of enol carbamates with 4-vinyl-1,3-dioxolan-2-one and allylic carbonates affords allylic alcohols and terminal allylated products, respectively. The assistance of the carbamoyl directing group provides a straightforward preparation of biologically and synthetically important allylated enol carbamates.



INTRODUCTION

The directing-group-assisted transition-metal-catalyzed C−H functionalization allows site-selective manipulation and offers an alternative to the traditional methods for the construction of C−C and C−X bonds.[1] In this context, the past decade has witnessed the C−H functionalization of (hetero)aromatic compounds with a range of chelating auxiliaries devised as effective directing groups. Recently, a great deal of effort has been devoted to the catalytic functionalization of vinylic C−H bonds[2] such as simple alkenes,[3a] acrylates,[3b] vinylic imines,[3c] acrylamides,[3d] enamides,[3e] enolates,[3f,g] and α-oxoketene dithioacetals.[3h] For instance, Loh et al. disclosed an elegant work on the Pd(II)-catalyzed cross-coupling reaction of simple alkenes with acrylates to afford (*E*)-2,4-dienoates.[3a] Miura and co-workers reported the synthesis of functionalized α-pyrones and butenolide derivatives by the rhodium-catalyzed oxidative coupling of substituted acrylic acids with alkynes and alkenes.[3b] Ellman and co-workers described the rhodium-catalyzed cascade reaction of vinylic imines and alkynes leading to dihydropyridine intermediates.[3c] In addition, Glorius et al. demonstrated the rhodium-catalyzed oxidative olefination of vinylic C−H bonds, including acrylates, acrylamides, and enamides, to deliver diunsaturated α-amino acids and linear 1,3-butadienes.[3e]

With the development of catalytic C−H bond functionalization, the directing-group-assisted C−H allylation reactions have been reported using various metal catalysts such as Rh, Ir, Ru, Pd, Re, Cu, Ni, and Co (Figure 1a).[4] For example, Glorius[4a] and Loh[4b] independently disclosed the direct C−H allylation of benzamides with allylic carbonates or allylic acetates via the Rh(III)-catalyzed olefin insertion and β-*O*-elimination pathway. In addition, Li and co-workers described the formation of β-branched amines and allylic alcohols through the Rh(III)-catalyzed C−H transformation of aromatic compounds with *N*-Ts aziridines[4f] and vinyl oxiranes.[4g] Furthermore, Wang et al. discovered the interesting allylation reaction of arenes with 4-vinyl-1,3-dioxolan-2-ones as coupling partners to yield (*E*)-allylic alcohols.[4h] In sharp contrast to aromatic C−H allylation

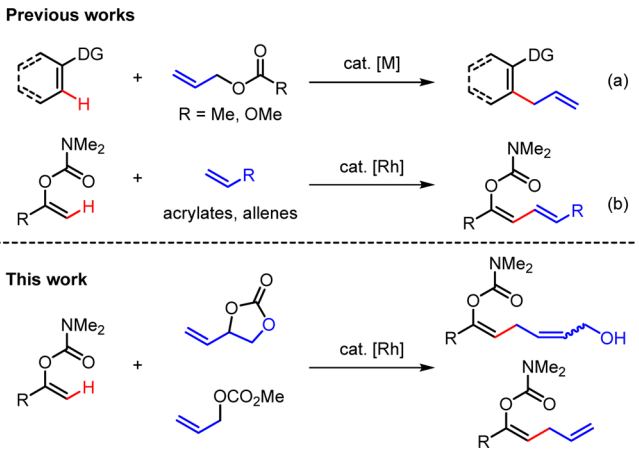


Figure 1. Direct allylation of sp^2 C−H bonds.

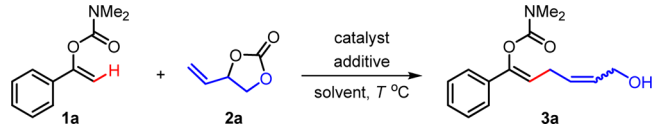
reactions, our group described the Ru(II)-catalyzed terminal allylation of vinylic C−H bonds on (hetero)aromatic and α,β-unsaturated carboxamides with allylic carbonates.[4i] Shortly thereafter, the Rh(III)-catalyzed C−H allylation of acrylamides with allylic acetates was also reported by Loh.[4j]

Enol carbamates have been recognized as integral structural motifs of pharmaceuticals and agrochemicals.[5] An enol carbamate moiety has also served as a versatile synthon for the formation of chiral alcohols via asymmetric hydrogenation,[6a] mandelic amides via α-alkylation, followed by [1,2]-Wittig rearrangement,[6b] and biaryl compounds via Suzuki−Miyaura cross-coupling reaction.[6c] However, the catalytic C−H functionalization of enol carbamates has been rarely exploited, and only two literatures were presented for the Rh(III)-catalyzed C−H olefination of enol carbamates with allenes and acrylates (Figure 1b).[3f,g] Our continued efforts on the rhodium-catalyzed C−H allylation reactions of aromatic

Received: November 6, 2015
Published: February 23, 2016

DOI: 10.1021/acs.joc.5b02562
J. Org. Chem. 2016, 81, 2243−2251

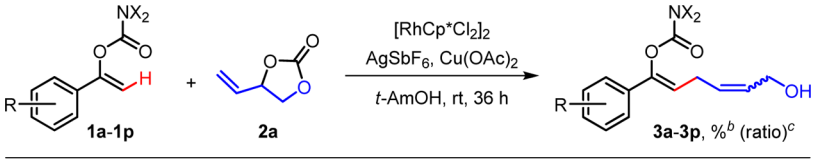
Table 1. Selected Optimization of Reaction Conditions[a]

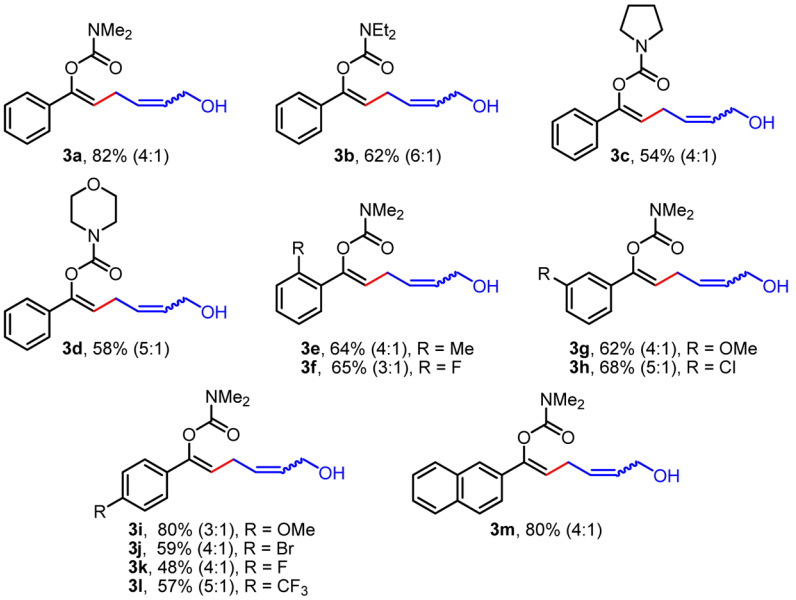


entry	catalyst (mol %)	additive (mol %)	solvent	yield (%),[b] ratio[c]
1	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10)	DCE	trace
2	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	DCE	44 (3:1)
3	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	THF	52 (3:1)
4	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	MeCN	39 (3:1)
5	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	toluene	41 (3:1)
6	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	*t*-AmOH	72 (3:1)
7	$[RuCl_2(p\text{-cymene})]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	*t*-AmOH	50 (1:1)
8	$[IrCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	*t*-AmOH	N.R.
9	$[CoCp^*COI_2]$ (5.0)	$AgSbF_6$ (10), $Cu(OAc)_2$ (100)	*t*-AmOH	N.R.
10	$[RhCp^*Cl_2]_2$ (2.5)	$Cu(OAc)_2$ (100)	*t*-AmOH	N.R.
11	$[RhCp^*Cl_2]_2$ (2.5)	$AgSbF_6$ (10), $Cu(OAc)_2$ (30)	*t*-AmOH	74 (4:1)
12[d]	**$[RhCp^*Cl_2]_2$ (2.5)**	**$AgSbF_6$ (10), $Cu(OAc)_2$ (30)**	***t*-AmOH**	**82 (4:1)**
13[d]	$[RhCp^*(MeCN)_3][SbF_6]_2$ (5.0)	$Cu(OAc)_2$ (30)	*t*-AmOH	76 (3:1)

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (quantity noted), additive (quantity noted), solvent (1 mL) at 60 °C for 24 h under air in reaction tubes. [b]Isolated yield by column chromatography. [c]Parentheses show ratio of *Z*/*Z*:*Z*/*E* isomers. [d]The reaction was performed at room temperature for 36 h.

Table 2. Scope of Enol Carbamates[a]

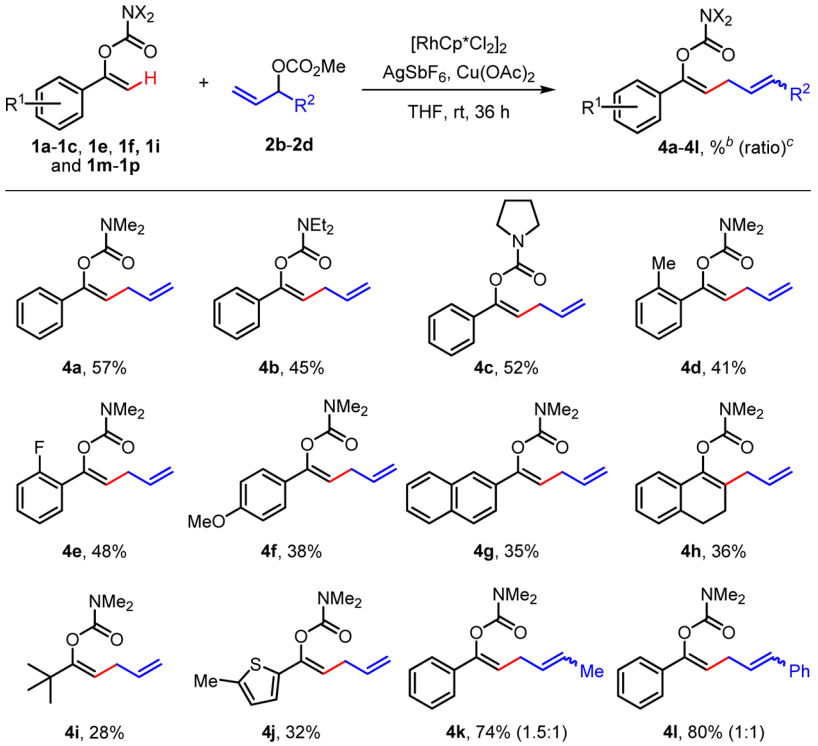




[a]Reaction conditions: **1a**−**1p** (0.2 mmol), **2a** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (30 mol %), *t*-AmOH (1 mL) at room temperature for 36 h under air in reaction tubes. [b]Isolated yield by flash column chromatography. [c]Ratio of *Z*/*Z*:*Z*/*E* isomers was determined by integral ratio in ^1H NMR.

DOI: 10.1021/acs.joc.5b02562
J. Org. Chem. 2016, 81, 2243−2251

Table 3. Scope of Allylic Carbonates with Enol Carbamates[a]



[a]Reaction conditions: **1a−1c**, **1e**, **1f**, **1i**, and **1m−1p** (0.2 mmol), **2b−2d** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (30 mol %), THF (1 mL) under air at room temperature for 36 h in reaction tubes. [b]Isolated yield by column chromatography. [c]Ratio of *Z*/*E*:*Z*/*Z* isomers was determined by integral ratio in ^1H NMR.

compounds[7] prompted us to explore the reaction of enol carbamates with allylic carbonates.

RESULTS AND DISCUSSION

In our initial study, 1-phenylvinyl dimethylcarbamate (**1a**) and 4-vinyl-1,3-dioxolan-2-one (**2a**) were chosen as model substrates for optimizing the reaction conditions, and selected results are summarized in Table 1. First, the cationic rhodium catalyst did not deliver our desired product **3a** in dichloroethane (DCE) at 60 °C (Table 1, entry 1). After extensive optimization, we found that a $Cu(OAc)_2$ additive plays a crucial role for the coupling of **1a** and **2a**, affording the allylic alcohol **3a** with a 3:1 *Z*/*Z*:*Z*/*E* isomeric ratio in 44% yield (Table 1, entry 2). Further screening of solvents revealed that *tert*-amyl alcohol (*t*-AmOH) was found to be an optimal solvent to furnish **3a** in 72% yield with no change of isomeric ratio (Table 1, entries 3−6). Next, we screened the well-known catalysts used for C−H allylation reactions such as Ru (entry 7),[4i] Ir (entry 8),[4d] and Co (entry 9).[4e] The cationic Ru catalyst promoted the coupling of **1a** and **2a** to give **3a** with slightly decreased reactivity and afforded a 1:1 stereoisomeric mixture. However, the cationic Ir and Co catalysts were found to be ineffective. In addition, no formation of **3a** was observed under neutral rhodium catalysis (Table 1, entry 10). To our pleasure, lowering the amount of copper additive to 30 mol % was found to be comparable in this transformation to provide **3a** in 74% yield (Table 1, entry 11). Interestingly, this reaction smoothly proceeded at ambient temperature to furnish the corresponding product **3a** in high yield, but no change of isomeric ratio was detected (Table 1, entry 12). In addition, the combination of isolable catalyst $[Cp^*Rh(MeCN)_3][SbF_6]_2$ and $Cu(OAc)_2$ provided a slightly decreased yield of **3a** (Table 1, entry 13).

With the optimized reaction conditions in hand, a range of enol carbamates **1b−1p** were tested to couple with **2a** (Table 2). Carbamoyl directing groups **1b−1d** such as diethyl, pyrrolidinyl, and morpholinyl were found to be coupled with **2a** to afford the corresponding allylic alcohol products **3b−3d** in moderate yields. However, in all cases, the regioisomeric ratio of allylic alcohols did not alter. In addition, *ortho*-, *meta*-, and *para*-substituted phenyl enol carbamates proved to be good substrates, providing **3e−3l**. Furthermore, this reaction proceeded with naphthyl enol carbamate **1m** to afford our desired product **3m** in 80% yield. However, *α*-substituted enol carbamate **1n** was less reactive under the present reaction conditions. Notably, this reaction was not limited to aryl enol carbamates. For example, alkyl and heteroaryl enol carbamates **1o** and **1p** also participated in this catalytic allylation reaction to furnish the allylic alcohols **3o** (65%) and **3p** (68%), respectively.

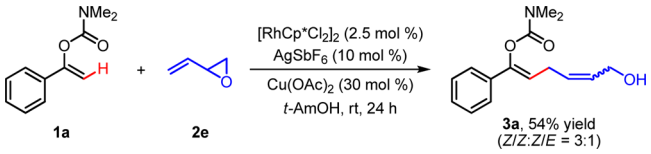
To explore the scope of other allylic carbonates, we performed the allylation reactions of **1a** with allyl methyl carbonate (**2b**) under the optimal reaction conditions. However, a trace amount of allylated product **4a** was formed under the optimized reaction conditions. After extensive optimization, we found that the coupling of **1a** and **2b** was effective in THF solvent under otherwise identical reaction conditions to give the terminal allylated product **4a** in 57% yield, as shown in Table 3. In addition, we screened other enol carbamates **1b** and **1c** with different carbonyl directing groups, but the corresponding allylated products **4b** and **4c** were formed in moderate yields. Even after lots of effort toward the optimization of reaction conditions, we were not able to increase the formation of our desired products **4a−4c**. At present, we are not sure about the exact reason behind this low

DOI: 10.1021/acs.joc.5b02562
J. Org. Chem. 2016, 81, 2243−2251

reactivity, but we believe that a terminal olefin of product under metal catalysis can undergo some side reactions.[8] Thus, we moved to the scope of enol carbamates with allylic carbonates. The reaction of aryl, alkyl, and heteroaryl enol carbamates with **2b** provided the corresponding terminal allylated products **4d**–**4j** in 28–48% yields. In sharp contrast to **2b**, the γ-substituted allylic carbonates **2c** and **2d** were smoothly allylated to give the crotylation products **4k** and **4l** in good yields with low isomeric ratio under the given reaction conditions. Notably, this reaction proceeded readily with complete γ-selectivity, and no migration of the double bond was observed.

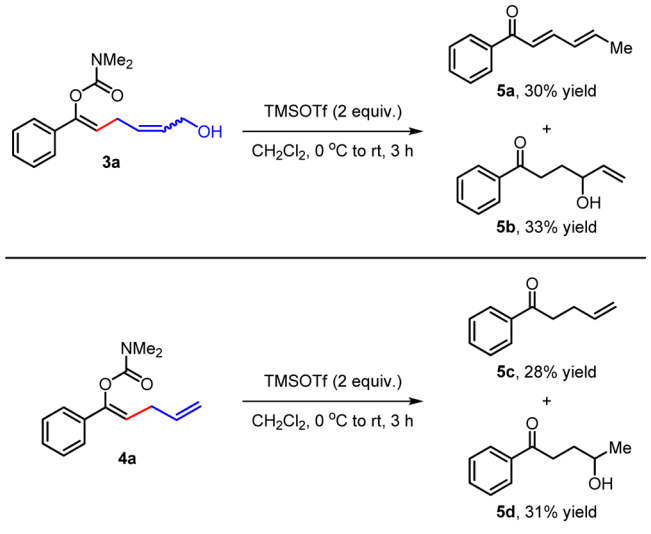
Next, we performed the coupling of 2-vinyloxirane (**2e**) with enol carbamate **1a** under the optimal reaction conditions to provide a mixture of allylic alcohol **3a** with a 3:1 regioisomeric ratio in 54% yield as a result of olefin insertion and epoxide ring-opening (Scheme 1).

Scheme 1. Allylation with 2-Vinyloxirane



To demonstrate the synthetic utility of allylated enol carbamates, the deprotection of **3a** and **4a** using TMSOTf was performed (Scheme 2).[9] Unexpectedly, allylic alcohol **3a** was converted into 2,4-dienone **5a** and branched allylic alcohol **5b**. Additionally, in contrast to deprotection of allylic alcohol **3a**, terminal allylated compound **4a** under the identical reaction conditions provided the corresponding ketone **5c** and unexpected hydrated compound **5d**.

Scheme 2. Deprotection of Enol Carbamates



Next, we found that the C–O bond of the enol carbamate moiety could be cleaved under nickel catalysis in the presence of phenylboronic acid,[3g] affording the corresponding arylated product **5e** (20%) in concomitant with olefin-migrated compound **5ea** (40%) (Scheme 3). In addition, we performed the Pd-catalyzed hydrogenation of allylic alcohol compound **3a** to give fully saturated product **5f** in 62% yield.

To obtain the mechanistic insight, we carried out two parallel reactions of **1a** and **deuterio-1a** with 4-vinyl-1,3-dioxolan-2-one (**2a**) under standard reaction conditions, which results in a kinetic isotope effect (k_H/k_D) of 1.6 (Scheme 4), thus indicating that C–H bond cleavage might not be involved in the rate-determining step.

A proposed reaction mechanism is depicted in Scheme 5. Coordination of a carbonyl group in enol carbamate **1a** to a cationic Rh(III) catalyst and subsequent C–H cleavage delivers the cyclorhodated intermediate **A**, which, on coordination and migratory insertion of **2a** into a Rh–C bond, affords an eight-membered Rh(III) intermediate **B** or **C**. On the basis of the experimental results, the *anti*-β-oxygen elimination of the intermediate **C** with the external acetoxy anion might be a more favorable pathway in the present context to provide the *cis*-isomer as a major product.[7a,10] Another pathway might be the *syn*-β-oxygen elimination of intermediate **B** to afford the *trans*-adduct. Both intermediates **B** and **C** release 1 mol of CO_2, and a Rh(III) catalyst can be regenerated in the catalytic cycle. Further, to examine the Rh-catalyzed isomerization of C=C double bonds, we performed the reaction of allylic alcohol **3e** with **2a** under the standard reaction conditions. No change of Z/E ratio was observed. This result supports that the formation of Z/E isomers might be generated by *anti*-β-oxygen elimination and *syn*-β-oxygen elimination.

CONCLUSION

In conclusion, we described the rhodium(III)-catalyzed direct C–H allylation of enol carbamates with allylic carbonates to afford allylic alcohols and terminal allylated products. With the assistance of the carbamoyl directing group, this protocol provides a straightforward and efficient method for the preparation of biologically and synthetically useful allylated enol carbamates.

EXPERIMENTAL SECTION

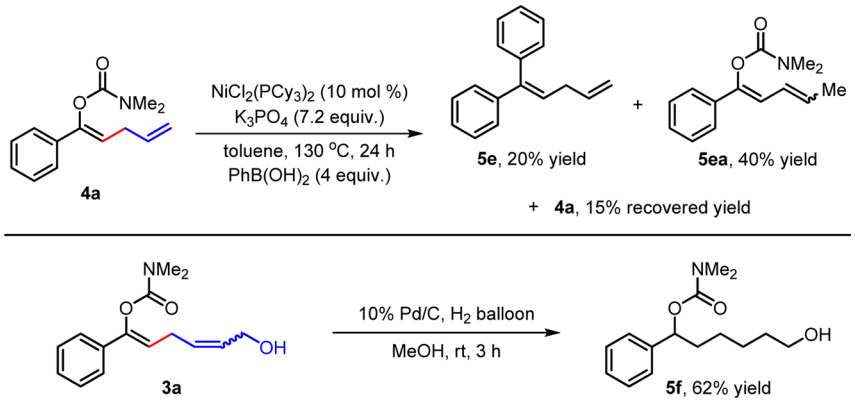
General Procedure for the Synthesis of Enol Carbamates.[3g] Sodium hydride (1.44 g, 36.0 mmol, 120 mol %, 60% suspension in oil) was added in portions to dry DMSO (60 mL). After stirring for 2 h at 50 °C, the resulting mixture was cooled to room temperature. Acetophenone (3.6 g, 30.0 mmol, 100 mol %) in DMSO (8 mL) was added dropwise into the reaction mixture. The reaction mixture was stirred for 15 min, and dimethylcarbamoyl chloride (3.32 mL, 36.0 mmol, 120 mol %) in DMSO (8 mL) was added dropwise. After stirring overnight, H_2O (60 mL) was added to the orange solution. The mixture was extracted with EtOAc (30 mL × 2), and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 10:1) to afford **1a** (2.8 g) in 49% yield as a colorless oil.

Typical Procedure for the Allylation of Enol Carbamates (3a–3p and 4a–4l). To an oven-dried sealed tube charged with 1-phenylvinyl dimethylcarbamate (**1a**) (38.2 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %), and $Cu(OAc)_2$ (10.8 mg, 0.06 mmol, 30 mol %) were added 4-vinyl-1,3-dioxolan-2-one (**2a**) (45.6 mg, 0.4 mmol, 200 mol %) and *t*-AmOH (1 mL). The reaction mixture was allowed to stir for 36 h at room temperature. The reaction mixture was diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 2:1) to afford **3a** (42.8 mg) in 82% yield as a light yellow oil.

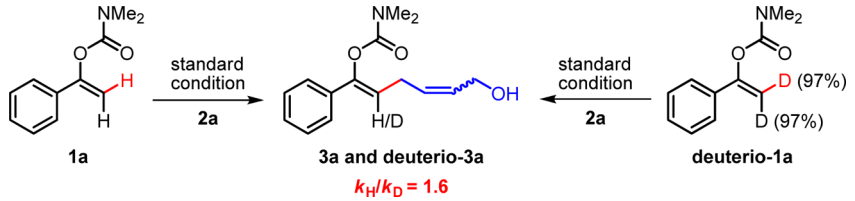
*(1Z,4Z)-6-Hydroxy-1-phenylhexa-1,4-dien-1-yl Dimethylcarbamate (**3a**).* 42.9 mg (82%); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 5.77 (t, J = 7.5 Hz, 1H), 5.69 (dtt, J = 11.0, 6.5, 1.0 Hz, 1H), 5.62 (dtt, J = 11.5, 7.5, 1.0 Hz, 1H), 4.19 (d, J = 6.5 Hz, 2H),

DOI: 10.1021/acs.joc.5b02562
J. Org. Chem. 2016, 81, 2243–2251

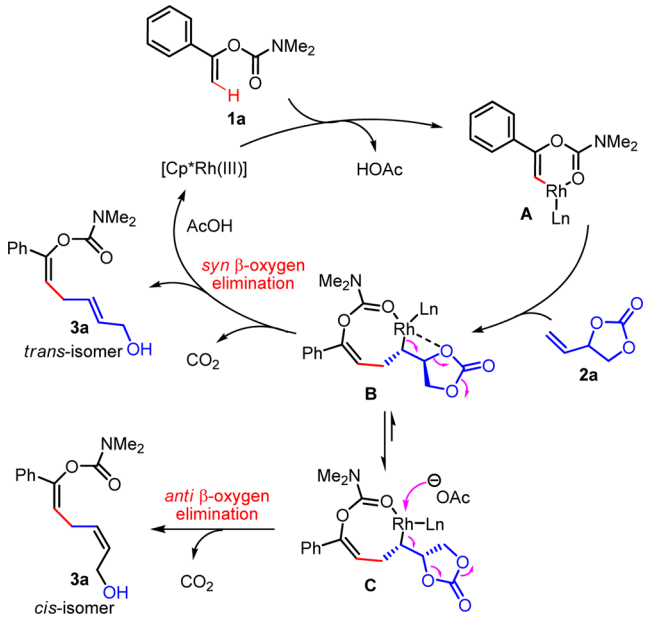
Scheme 3. Transformation of Allylated Products



Scheme 4. Kinetic Isotope Effect Experiments



Scheme 5. Proposed Reaction Pathway



3.16 (s, 3H), 2.99 (s, 3H), 2.97 (t, J = 7.5 Hz, 2H), 1.74 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 146.5, 135.4, 129.5, 129.1, 128.4, 128.1, 124.4, 115.4, 58.0, 36.7, 36.4, 24.6; IR (KBr) υ 3415, 2929, 2863, 1702, 1624, 1445, 1392, 1262, 1162, 1060, 755, 690 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{15}H_{20}NO_3$ $[M + H]^+$ 262.1443, found 262.1440

*(1Z,4Z)-6-Hydroxy-1-phenylhexa-1,4-dien-1-yl Diethylcarbamate (**3b**).* 35.8 mg (62%); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.0 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 5.76 (t, J = 7.0 Hz, 1H), 5.70 (dtt, J = 11.0, 6.5, 1.5 Hz, 1H), 5.62 (dtt, J = 11.0, 7.5, 1.0 Hz, 1H), 4.18 (d, J = 6.5 Hz, 2H), 3.51 (q, J = 7.0 Hz, 2H), 3.37 (q, J = 7.0 Hz, 2H), 2.96 (t, J = 7.0 Hz, 2H), 1.76 (br s, 1H), 1.30 (t, J = 7.0 Hz, 3H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 146.6, 135.6, 129.6, 129.2, 128.4, 128.0, 124.5, 115.5, 58.0, 42.1, 41.8, 24.6, 14.4, 13.3; IR (KBr) υ 3414, 2930, 2874, 1698, 1599, 1422, 1379, 1257, 1157, 1067, 755, 691 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{17}H_{23}NO_3$ $[M]^+$ 289.1678, found 289.1671.

*(1Z,4Z)-6-Hydroxy-1-phenylhexa-1,4-dien-1-yl Pyrrolidine-1-carboxylate (**3c**).* 31.1 mg (54%); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.27–7.24 (m, 1H), 5.82 (t, J = 7.5 Hz, 1H), 5.69 (dtt, J = 11.0, 7.0, 1.0 Hz, 1H), 5.63 (dtt, J = 11.0, 7.5, 1.0 Hz, 1H), 4.17 (d, J = 7.0 Hz, 2H), 3.62 (t, J = 6.5 Hz, 2H), 3.46 (t, J = 7.0 Hz, 2H), 2.97 (t, J = 7.5 Hz, 2H), 2.09–1.97 (m, 2H), 1.96–1.90 (m, 2H), 1.86 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7, 146.4, 135.5, 129.4, 129.1, 128.4, 128.1, 124.5, 115.4, 58.0, 46.5, 46.4, 25.8, 24.9, 24.7; IR (KBr) υ 3422, 2923, 2873, 1715, 1613, 1408, 1271, 1175, 1083, 913, 757, 697 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{17}H_{22}NO_3$ $[M + H]^+$ 288.1600, found 288.1598.

*(1Z,4Z)-6-Hydroxy-1-phenylhexa-1,4-dien-1-yl Morpholine-4-carboxylate (**3d**).* 35.2 mg (58%); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.37 (m, 2H), 7.34–7.27 (m, 3H), 5.79 (t, J = 7.4 Hz, 1H), 5.71 (dtt, J = 10.5, 6.8, 1.5 Hz, 1H), 5.62 (dtt, J = 11.0, 6.8, 1.0 Hz, 1H), 4.19 (d, J = 6.8 Hz, 2H), 3.75 (br s, 8H), 2.96 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 146.4, 135.1, 129.5, 129.0, 128.5, 128.3, 124.3, 115.6, 66.6, 58.0, 44.9, 44.2, 24.6; IR (KBr) υ 3440, 2924, 2856, 1718, 1428, 1365, 1230, 1115, 1071, 758, 698 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{17}H_{22}NO_4$ $[M + H]^+$ 304.1549, found 304.1546.

*(1Z,4Z)-6-Hydroxy-1-(o-tolyl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3e**).* 35.3 mg (64%); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.0 Hz, 1H), 7.21–7.13 (m, 3H), 5.69 (dtt, J = 11.0, 6.5, 1.0 Hz, 1H), 5.63 (dtt, J = 11.0, 7.0, 1.0 Hz, 1H), 5.28 (t, J = 7.5 Hz, 1H), 4.20 (d, J = 6.5 Hz, 2H), 3.05 (s, 3H), 2.97 (t, J = 7.5 Hz, 2H), 2.87 (s, 3H), 2.41 (s, 3H), 2.01 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 146.9, 136.0, 135.9, 130.3, 129.5, 129.4, 129.2, 128.2, 125.5, 118.7, 58.0, 36.6, 36.3, 24.4, 20.2; IR (KBr) υ 3423, 2925, 2855, 1716, 1455, 1393, 1258, 1168, 1061, 867, 757 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{16}H_{21}NO_3$ $[M]^+$ 275.1521, found 275.1526.

*(1Z,4Z)-1-(2-Fluorophenyl)-6-hydroxyhexa-1,4-dien-1-yl Dimethylcarbamate (**3f**).* 36.3 mg (65%); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.31 (m, 1H), 7.24–7.21 (m, 1H), 7.09 (t, J = 7.5 Hz, 1H), 7.05–7.01 (m, 1H), 5.85 (t, J = 7.5 Hz, 1H), 5.69 (dtt, J = 10.5, 7.5, 1.5 Hz, 1H), 5.62 (dtt, J = 11.0, 7.5, 1.0 Hz, 1H), 4.19 (d, J = 7.0 Hz, 2H), 3.12 (s, 3H), 2.98–2.95 (m, 5H), 1.72 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (d, $J_{C\text{-}F}$ = 249.1 Hz),

DOI: 10.1021/acs.joc.5b02562
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154.2, 141.7 (d, J_{C-F} = 3.5 Hz), 130.2, 129.6, 129.4 (d, J_{C-F} = 8.2 Hz), 129.1, 128.1 (d, J_{C-F} = 2.7 Hz), 124.0 (d, J_{C-F} = 3.5 Hz), 120.4 (d, J_{C-F} = 8.2 Hz), 116.1 (d, J_{C-F} = 22.7 Hz), 58.1, 36.7, 36.4, 24.7; IR (KBr) υ 3423, 2924, 2855, 1719, 1612, 1451, 1395, 1261, 1168, 1059, 866, 757, 698 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{18}FNO_3$ $[M]^+$ 279.1271, found 279.1272.

*(1Z,4Z)-6-Hydroxy-1-(3-methoxyphenyl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3g**).* 36.1 mg (62%); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.93 (s, 1H), 6.82−6.80 (m, 1H), 5.81−5.58 (m, 3H), 4.17 (d, J = 6.7 Hz, 2H), 3.80 (s, 3H), 3.15 (s, 3H), 2.98−2.94 (m, 5H), 1.75 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.2, 146.4, 136.9, 129.5, 129.1, 117.0, 115.7, 115.4, 113.4, 110.4, 58.0, 55.2, 36.8, 36.4, 24.6; IR (KBr) υ 3414, 2924, 2854, 1715, 1600, 1579, 1487, 1394, 1260, 1166, 1040, 873, 783, 690 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{22}NO_4$ $[M + H]^+$ 292.1549, found 292.1551.

*(1Z,4Z)-1-(3-Chlorophenyl)-6-hydroxyhexa-1,4-dien-1-yl Dimethylcarbamate (**3h**).* 40.2 mg (68%); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.29−7.23 (m, 3H), 5.80 (t, J = 7.2 Hz, 1H), 5.73−5.57 (m, 2H), 4.17 (d, J = 6.8 Hz, 2H), 3.16 (s, 3H), 2.99 (s, 3H), 2.97−2.90 (m, 2H), 1.80 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 145.4, 137.3, 134.4, 129.8, 129.7, 128.7, 128.1, 124.6, 122.6, 116.8, 58.0, 36.8, 36.4, 24.6; IR (KBr) υ 3435, 2922, 2855, 1718, 1595, 1457, 1393, 1258, 1166, 1069, 821, 759 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{18}ClNO_3$ $[M]^+$ 295.0975, found 295.0977.

*(1Z,4Z)-6-Hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3i**).* 46.6 mg (80%); Light brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.68−5.62 (m, 3H), 4.17 (d, J = 6.6 Hz, 2H), 3.78 (s, 3H), 3.15 (s, 3H), 2.96 (s, 3H), 2.94 (d, J = 7.3 Hz, 2H), 2.00 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 154.3, 146.3, 129.4, 129.3, 128.1, 125.8, 113.8, 113.5, 58.0, 55.2, 36.7, 36.4, 24.5; IR (KBr) υ 3398, 2924, 2853, 1714, 1600, 1509, 1461, 1392, 1249, 1165, 1027, 839, 757 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{22}NO_4$ $[M + H]^+$ 292.1543, found 292.1546.

*(1Z,4Z)-1-(4-Bromophenyl)-6-hydroxyhexa-1,4-dien-1-yl Dimethylcarbamate (**3j**).* 40.1 mg (59%); Light brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 5.79 (t, J = 7.5 Hz, 1H), 5.69 (dtt, J = 10.5, 7.0, 1.5 Hz, 1H), 5.61 (dtt, J = 11.0, 7.5, 1.0 Hz, 1H), 4.17 (d, J = 6.8 Hz, 2H), 3.14 (s, 3H), 2.99 (s, 3H), 2.97−2.89 (m, 2H), 1.77 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 145.7, 134.5, 131.6, 129.6, 128.9, 126.0, 122.1, 116.1, 58.0, 36.8, 36.4, 24.6; IR (KBr) υ 3415, 2925, 2857, 1713, 1586, 1485, 1389, 1261, 1161, 1006, 816, 755, 658 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{18}BrNO_3$ $[M]^+$ 339.0470, found 339.0477.

*(1Z,4Z)-1-(4-Fluorophenyl)-6-hydroxyhexa-1,4-dien-1-yl Dimethylcarbamate (**3k**).* 26.8 mg (48%); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (m, 2H), 7.02−6.97 (m, 2H), 5.72−5.59 (m, 3H), 4.16 (d, J = 6.7 Hz, 2H), 3.15 (s, 3H), 2.98 (s, 3H), 2.96−2.89 (m, 2H), 2.04 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J_{C-F} = 246.2 Hz), 154.2, 145.8, 131.7 (d, J_{C-F} = 3.3 Hz), 129.5, 129.0, 126.2 (d, J_{C-F} = 32.5 Hz), 115.5, 115.3 (d, J_{C-F} = 17.0 Hz), 58.0, 36.8, 36.4, 24.5; IR (KBr) υ 3403, 2923, 2854, 1714, 1621, 1508, 1455, 1393, 1226, 1155, 1060, 842, 757 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{18}FNO_3$ $[M]^+$ 279.1271, found 279.1275.

*(1Z,4Z)-6-Hydroxy-1-(4-(trifluoromethyl)phenyl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3l**).* 37.5 mg (57%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 5.86 (t, J = 7.4 Hz, 1H), 5.74−5.68 (m, 1H), 5.64−5.58 (m, 1H), 4.19 (d, J = 6.9 Hz, 2H), 3.17 (s, 3H), 3.00−2.97 (m, 5H), 1.80 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 145.6, 139.0, 130.5, 129.9, 128.6, 125.4 (q, J_{C-F} = 3.7 Hz), 124.7, 124.0 (q, J_{C-F} = 270.6 Hz), 117.8, 58.1, 36.8, 36.4, 24.6; IR (KBr) υ 3423, 2924, 2854, 1714, 1617, 1454, 1323, 1265, 1114, 1067, 829, 759, 699 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{19}F_3NO_3$ $[M + H]^+$ 330.1317, found 330.1318.

*(1Z,4Z)-6-Hydroxy-1-(naphthalen-2-yl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3m**).* 49.8 mg (80%); Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.81−7.73 (m, 4H), 7.56 (dd, J = 8.5, 2.0 Hz, 1H), 7.46−7.43 (m, 2H), 5.91 (t, J = 7.5 Hz, 1H), 5.72 (dtt, J = 10.5, 7.0, 1.0 Hz, 1H), 5.66 (dtt, J = 11.0, 7.5, 1.0 Hz, 1H), 4.21 (d, J = 6.5 Hz, 2H), 3.23 (s, 3H), 3.02−2.95 (m, 5H), 1.80 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 146.7, 133.2, 133.1, 132.8, 129.6, 129.1, 128.3, 128.2, 127.5, 126.2, 126.1, 123.4, 122.6, 116.1, 58.1, 36.8, 36.5, 24.7; IR (KBr) υ 3400, 2926, 2857, 1715, 1625, 1598, 1453, 1395, 1266, 1169, 1053, 818, 754 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{19}H_{22}NO_3$ $[M + H]^+$ 312.1600, found 312.1600.

*(Z)-2-(4-Hydroxybut-2-en-1-yl)-3,4-dihydronaphthalen-1-yl Dimethylcarbamate (**3n**).* 16.1 mg (28%); Light brown oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15−7.08 (m, 3H), 7.03 (d, J = 7.1 Hz, 1H), 5.75−5.59 (m, 2H), 4.18 (d, J = 6.8 Hz, 2H), 3.17 (s, 3H), 3.02 (s, 3H), 3.01−2.97 (m, 2H), 2.87−2.83 (m, 2H), 2.42−2.38 (m, 2H), 1.75 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 140.4, 135.4, 131.6, 130.0, 128.4, 127.2, 127.1, 126.4, 125.8, 120.4, 58.1, 36.8, 36.4, 28.8, 27.6, 26.6; IR (KBr) υ 3414, 2924, 2854, 1715, 1600, 1579, 1487, 1394, 1260, 1166, 1040, 873, 783, 690 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{17}H_{21}NO_3$ $[M]^+$ 287.1521, found 287.1524.

*(3Z,6Z)-8-Hydroxy-2,2-dimethylocta-3,6-dien-3-yl Dimethylcarbamate (**3o**).* 31.4 mg (65%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.67−5.62 (m, 1H), 5.53−5.50 (m, 1H), 5.06 (t, J = 7.5 Hz, 1H), 4.09 (t, J = 7.5 Hz, 2H), 3.03 (s, 3H), 2.97 (s, 3H), 2.68 (t, J = 7.5 Hz, 2H), 2.12 (br s, 1H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 154.5, 130.1, 128.7, 111.1, 57.8, 36.7, 36.3, 36.1, 27.9, 24.5; IR (KBr) υ 3448, 2961, 2870, 1705, 1459, 1389, 1269, 1167, 1070, 970, 865, 755 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{23}NO_3$ $[M]^+$ 241.1678, found 241.1681.

*(1Z,4Z)-6-Hydroxy-1-(5-methylthiophen-2-yl)hexa-1,4-dien-1-yl Dimethylcarbamate (**3p**).* 38.2 mg (68%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 6.77 (d, J = 3.5 Hz, 1H), 6.58 (d, J = 3.5 Hz, 2H), 5.67 (dtt, J = 10.5, 7.0, 1.5 Hz, 1H), 5.62−5.55 (m, 2H), 4.16 (d, J = 7.5 Hz, 2H), 3.12 (s, 3H), 3.00 (s, 3H), 2.90 (t, J = 7.5 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 141.8, 139.5, 136.9, 129.4, 128.9, 125.5, 123.2, 113.8, 58.0, 36.8, 36.4, 24.4, 15.3; IR (KBr) υ 3415, 2922, 2857, 1709, 1660, 1452, 1394, 1257, 1164, 1060, 943, 799, 698 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{14}H_{20}NO_3S$ $[M + H]^+$ 282.1164, found 282.1160.

*(Z)-1-Phenylpenta-1,4-dien-1-yl Dimethylcarbamate (**4a**).* 26.4 mg (57%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 7.5 Hz, 1H), 5.88 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.80 (t, J = 7.5 Hz, 1H), 5.13 (dq, J = 17.0, 2.0 Hz, 1H), 5.04 (dq, J = 10.0, 2.0 Hz, 1H), 3.14 (s, 3H), 2.97 (s, 3H), 2.94 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 147.1, 135.8, 135.6, 128.3, 127.9, 124.4, 115.4, 115.2, 36.7, 36.3, 30.3; IR (KBr) υ 3059, 2930, 1717, 1638, 1493, 1390, 1262, 1160, 1062, 914, 862, 755, 690 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338, found 232.1333.

*(Z)-1-Phenylpenta-1,4-dien-1-yl Diethylcarbamate (**4b**).* 23.3 mg (45%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 8.5 Hz, 2H), 7.25 (t, J = 7.5 Hz, 1H), 5.88 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.80 (t, J = 7.5 Hz, 1H), 5.12 (dq, J = 17.0, 2.0 Hz, 1H), 5.03 (dq, J = 10.0, 2.0 Hz, 1H), 3.46 (q, J = 7.0 Hz, 2H), 3.35 (q, J = 7.0 Hz, 2H), 2.95−2.92 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.3, 147.1, 135.9, 135.8, 128.3, 127.9, 124.4, 115.4, 115.1, 42.1, 41.8, 30.4, 14.4, 13.3; IR (KBr) υ 3059, 2975, 2875, 1713, 1638, 1419, 1254, 1153, 1065, 992, 753, 690 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{22}NO_2$ $[M + H]^+$ 260.1651, found 260.1645.

*(Z)-1-Phenylpenta-1,4-dien-1-yl Pyrrolidine-1-carboxylate (**4c**).* 26.8 mg (52%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45−7.43 (m, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.27−7.23 (m, 1H), 5.89 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.80 (t, J = 7.0 Hz, 1H), 5.13 (dq, J = 17.0, 2.0 Hz, 1H), 5.04 (dq, J = 10.0, 1.5 Hz, 1H), 3.60 (t, J = 7.0 Hz, 2H), 3.44 (t, J = 7.0 Hz, 2H), 2.97−2.94 (m, 2H), 2.02−1.96 (m, 2H), 1.94−1.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 146.9, 135.9, 135.8, 128.3, 127.9, 124.5, 115.4, 115.3, 46.4, 46.3, 30.4, 25.8, 24.9; IR (KBr) υ 3059, 2975, 2876, 1715, 1637, 1402, 1270, 1173,

DOI: 10.1021/acs.joc.5b02562
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1079, 911, 754, 691 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1494, found 258.1493.

*(Z)-1-(o-Tolyl)penta-1,4-dien-1-yl Dimethylcarbamate (**4d**).* 20.1 mg (41%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38−7.36 (m, 1H), 7.21−7.14 (m, 3H), 5.89 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.31 (t, J = 7.0 Hz, 1H), 5.13 (dq, J = 17.0, 2.0 Hz, 1H), 5.04 (dq, J = 10.0, 1.5 Hz, 1H), 3.05 (s, 3H), 2.97 (t, J = 7.5 Hz, 2H), 2.89 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9, 147.4, 136.4, 136.0, 135.8, 130.2, 129.1, 128.1, 125.5, 118.2, 115.2, 36.4, 36.2, 30.0, 20.3; IR (KBr) υ 3019, 2925, 1717, 1638, 1455, 1389, 1257, 1159, 1055, 908, 866, 754, 698 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{15}H_{20}NO_2$ $[M + H]^+$ 246.1494, found 246.1493.

*(Z)-1-(2-Fluorophenyl)penta-1,4-dien-1-yl Dimethylcarbamate (**4e**).* 24.0 mg (48%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (td, J = 8.0, 2.0 Hz, 1H), 7.25−7.20 (m, 1H), 7.09 (td, J = 7.5, 1.5 Hz, 1H), 7.05−7.01 (m, 1H), 5.88 (ddt, J = 17.0, 10.5, 6.0 Hz, 1H), 5.84 (t, J = 7.5 Hz, 1H), 5.14 (dq, J = 17.0, 2.0 Hz, 1H), 5.05 (dq, J = 10.0, 1.5 Hz, 1H), 3.10 (s, 3H), 2.97−2.95 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5 (d, $J_{C\text{-}F}$ = 249.1 Hz), 154.0, 142.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 135.6, 129.3 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 124.0 (d, $J_{C\text{-}F}$ = 3.5 Hz), 120.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 116.2 (d, $J_{C\text{-}F}$ = 22.6 Hz), 115.5, 36.7, 36.3, 30.3; IR (KBr) υ 3079, 2926, 2855, 1717, 1638, 1488, 1390, 1255, 1155, 1061, 912, 832, 755 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{14}H_{16}FNO_2$ $[M]^+$ 249.1165, found 249.1161.

*(Z)-1-(4-Methoxyphenyl)penta-1,4-dien-1-yl Dimethylcarbamate (**4f**).* 19.9 mg (38%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.88 (ddt, J = 17.0, 10.5, 6.0 Hz, 1H), 5.66 (t, J = 7.3 Hz, 1H), 5.13 (dq, J = 17.1, 1.6 Hz, 1H), 5.02 (dq, J = 10.0, 1.3 Hz, 1H), 3.79 (s, 3H), 3.13 (s, 3H), 2.97 (s, 3H), 2.91 (t, J = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 154.1, 146.9, 136.1, 128.5, 125.8, 115.2, 113.8, 113.4, 55.2, 36.7, 36.4, 30.3; IR (KBr) υ 3003, 2931, 2837, 1716, 1606, 1509, 1455, 1389, 1246, 1158, 1029, 912, 826, 755, 698 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{19}NO_3$ $[M]^+$ 261.1365, found 261.1363.

*(Z)-1-(Naphthalen-2-yl)penta-1,4-dien-1-yl Dimethylcarbamate (**4g**).* 19.7 mg (35%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82−7.77 (m, 4H), 7.59 (dd, J = 8.5, 2.0 Hz, 1H), 7.47−7.42 (m, 2H), 5.95 (t, J = 7.2 Hz, 1H), 5.92 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.18 (dq, J = 17.0, 2.0 Hz, 1H), 5.07 (dq, J = 10.0, 1.5 Hz, 1H), 3.21 (s, 3H), 3.00−2.98 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 147.2, 135.8, 133.2, 133.1, 133.0, 128.3, 128.1, 127.5, 126.2, 126.0, 123.3, 122.7, 115.9, 115.6, 36.8, 36.5, 30.5; IR (KBr) υ 3056, 2925, 1715, 1637, 1505, 1446, 1390, 1266, 1156, 1060, 910, 812, 750, 673 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{18}H_{19}NO_2$ $[M]^+$ 281.1416, found 281.1416.

*2-Allyl-3,4-dihydronaphthalen-1-yl Dimethylcarbamate (**4h**).* 18.5 mg (36%); Light brown oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16−7.12 (m, 1H), 7.11−7.09 (m, 2H), 7.06−7.05 (m, 1H), 5.81 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 5.13 (dq, J = 17.0, 1.5 Hz, 1H), 5.06 (dq, J = 10.0, 1.5 Hz, 1H), 3.16 (s, 3H), 3.00 (s, 3H), 2.92 (d, J = 6.6 Hz, 2H), 2.85 (t, J = 7.9 Hz, 2H), 2.37 (t, J = 8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.5, 140.8, 135.6, 135.0, 131.8, 127.1, 126.9, 126.3, 125.5, 120.4, 116.3, 36.7, 36.4, 35.2, 27.7, 26.5; IR (KBr) υ 3068, 2931, 2884, 1716, 1636, 1486, 1387, 1270, 1152, 1072, 997, 849, 757 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{16}H_{20}NO_2$ $[M + H]^+$ 258.1494, found 258.1493.

*(Z)-2,2-Dimethylhepta-3,6-dien-3-yl Dimethylcarbamate (**4i**).* 11.9 mg (28%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 5.08 (t, J = 7.0 Hz, 1H), 5.02 (dq, J = 17.0, 1.5 Hz, 1H), 4.95 (dq, J = 10.0, 1.5 Hz, 1H), 3.02 (s, 3H), 2.95 (s, 3H), 2.64 (t, J = 8.0 Hz, 2H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 154.1, 136.7, 114.7, 110.9, 36.7, 36.2, 36.1, 30.2, 28.0; IR (KBr) υ 3077, 2965, 2870, 1720, 1677, 1459, 1386, 1270, 1164, 1078, 908, 864, 754 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{12}H_{21}NO_2$ $[M]^+$ 211.1572, found 211.1579.

*(Z)-1-(5-Methylthiophen-2-yl)penta-1,4-dien-1-yl Dimethylcarbamate (**4j**).* 16.1 mg (32%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, J = 3.4 Hz, 1H), 6.58 (d, J = 2.8 Hz, 1H), 5.84 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 5.61 (t, J = 7.4 Hz, 1H), 5.10 (dq, J = 17.0, 1.5 Hz, 1H), 5.02 (dq, J = 10.0, 1.5 Hz, 1H), 3.10 (s, 3H), 2.98 (s, 3H), 2.87 (t, J = 6.7 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 142.3, 139.3, 137.2, 135.7, 125.4, 123.2, 115.4, 113.8, 36.7, 36.4, 30.1, 15.3; IR (KBr) υ 3075, 2923, 2855, 1724, 1637, 1446, 1390, 1256, 1161, 1064, 918, 860, 798 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{17}NO_2S$ $[M]^+$ 251.0980, found 251.0975.

*(1Z,4Z)-1-Phenylhexa-1,4-dien-1-yl Dimethylcarbamate and (1Z,4E)-1-Phenylhexa-1,4-dien-1-yl Dimethylcarbamate (**4k**).* 36.3 mg (74%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) **(1Z,4Z)-isomer**: δ 7.37−7.35 (m, 2H), 7.27−7.24 (m, 2H), 7.21−7.18 (m, 1H), 5.73 (t, J = 7.0 Hz, 1H), 5.52−5.38 (m, 2H), 3.10 (s, 3H), 2.93 (s, 3H), 2.88 (t, J = 7.0 Hz, 2H), 1.62 (d, J = 7.0 Hz, 3H); **(1Z,4E)-isomer**: δ 7.37−7.35 (m, 2H), 7.27−7.24 (m, 2H), 7.21−7.18 (m, 1H), 5.70 (t, J = 7.5 Hz, 1H), 5.52−5.38 (m, 2H), 3.09 (s, 3H), 2.93 (s, 3H), 2.81 (t, J = 7.0 Hz, 2H), 1.61 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.1, 146.5, 135.8, 135.7, 128.3, 128.2, 127.8, 127.3, 126.1, 125.0, 124.5, 124.4, 116.4, 116.3, 36.7, 36.4, 29.2, 24.0, 17.8, 12.7; IR (KBr) υ 3019, 2925, 1717, 1638, 1455, 1389, 1257, 1159, 1055, 908, 866, 754, 698 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{15}H_{19}NO_2$ $[M]^+$ 245.1416, found 245.1416.

*(1Z,4E)-1,5-Diphenylpenta-1,4-dien-1-yl Dimethylcarbamate and (1Z,4Z)-1,5-Diphenylpenta-1,4-dien-1-yl Dimethylcarbamate (**4l**).* 49.2 mg (80%); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.41 (m, 4H), 7.38−7.26 (m, 13H), 7.25−7.19 (m, 3H), 6.53−6.46 (m, 2H), 6.31−6.23 (m, 1H), 5.88 (t, J = 7.2 Hz, 1H), 5.85 (t, J = 6.4 Hz, 1H), 5.74 (dt, J = 11.4, 7.5 Hz, 1H), 3.22 (td, J = 7.4, 1.7 Hz, 2H), 3.15 (s, 3H), 3.11 (td, J = 7.2, 1.4 Hz, 2H), 3.02 (s, 3H), 2.97 (s, 3H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 154.0, 147.2, 147.1, 137.4, 137.1, 135.7, 135.6, 130.8, 129.7, 129.2, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.0, 126.6, 126.0, 124.5, 124.4, 115.6, 115.2, 36.7, 36.6, 36.4, 36.2, 29.6, 25.6; IR (KBr) υ 3003, 2931, 2837, 1716, 1606, 1509, 1455, 1389, 1246, 1158, 1029, 912, 826, 755, 698 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{21}NO_2$ $[M]^+$ 307.1572, found 307.1571.

General Procedure and Characterization Data for the Cleavage of Carbomoyl Group. To an oven-dried sealed tube charged with allylic alcohol **3a** (52.2 mg, 0.2 mmol, 100 mol %) in CH_2Cl_2 (2 mL) was added TMSOTf (73 μL, 0.4 mmol, 200 mol %) at 0 °C under a N_2 atmosphere. The reaction mixture was allowed to stir for 1 h at 0 °C, and further stirred for 2 h at room temperature. The reaction mixture was quenched with H_2O (3 mL) and was extracted with EtOAc (5 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 80:1 to 10:1) to afford **5a** (10.3 mg, 30% yield) and **5b** (12.5 mg, 33% yield).

*(2E,4E)-1-Phenylhexa-2,4-dien-1-one (**5a**).* 10.3 mg (30%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.43−7.37 (m, 1H), 6.88 (d, J = 15.0 Hz, 1H), 6.37−6.35 (m, 2H), 1.91 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.9, 145.2, 141.1, 138.3, 132.5, 130.6, 128.5, 128.3, 18.9; IR (KBr) υ 3060, 2923, 2853, 1661, 1589, 1447, 1339, 1257, 1014, 929, 760, 697 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{12}H_{12}O$ $[M]^+$ 172.0888, found 172.0884.

*4-Hydroxy-1-phenylhex-5-en-1-one (**5b**).* 12.5 mg (33%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 5.94−5.88 (m, 1H), 5.27 (dt, J = 17.5, 1.5 Hz, 1H), 5.15 (dt, J = 10.5, 1.5 Hz, 1H), 4.25 (q, J = 6.0 Hz, 1H), 3.13 (t, J = 7.0 Hz, 1H), 2.09−1.91 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 140.7, 136.8, 133.1, 128.5, 128.0, 114.9, 72.2, 34.3, 30.8; IR (KBr) υ 3425, 2924, 2854, 1680, 1596, 1448, 1320, 1262, 1179, 1047, 991, 742, 689 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{12}H_{14}O_2$ $[M]^+$ 190.0994, found 190.1001.

*1-Phenylpent-4-en-1-one (**5c**).* 9.0 mg (28%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 5.91 (ddt, J = 17.0, 10.5, 6.5 Hz, 1H), 5.09 (dq, J = 17.0, 1.5 Hz, 1H), 5.01 (dq, J = 10.0, 1.5 Hz, 1H), 3.08 (t, J = 7.5 Hz, 2H), 2.52−2.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 137.3, 136.9, 133.0, 128.5, 128.0, 115.2, 37.7, 28.1; IR (KBr) 3065, 2923, 2853, 1885, 1641, 1597, 1448, 1206, 1179, 1000,

DOI: 10.1021/acs.joc.5b02562
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913, 743, 689 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{11}H_{13}O$ $[M + H]^+$ 161.0966, found 161.0962.

*4-Hydroxy-1-phenylpentan-1-one (**5d**).* 11.1 mg (31%); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.0 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 3.92−3.84 (m, 1H), 3.14 (br s, 2H), 1.98−1.90 (m, 1H), 1.87−1.82 (m, 2H), 1.25 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.7, 136.8, 133.0, 128.5, 128.1, 67.5, 34.9, 33.0, 23.8; IR (KBr) υ 3060, 2924, 2853, 1715, 1686, 1599, 1450, 1315, 1274, 1111, 1071, 713, 698 cm^{-1}; HRMS (orbitrap, ESI) calcd for $C_{11}H_{15}O_2$ $[M + H]^+$ 179.1072, found 179.1068.

Experimental Procedure and Characterization Data for the Ni-Catalyzed Arylation of 4a. To an oven-dried sealed tube charged with **4a** (80.9 mg, 0.35 mmol, 100 mol %), $NiCl_2(PCy_3)_2$ (24.2 mg, 0.035 mmol, 10 mol %), and K_3PO_4 (534.9 mg, 2.52 mmol, 7.2 equiv) in toluene (2 mL) was added phenylboronic acid (170.7 mg, 1.4 mmol, 400 mol %) at room temperature under a N_2 atmosphere. The reaction mixture was allowed to stir for 1 h at 230 °C, and further stirred for 24 h at 130 °C. The resulting mixture was quenched with H_2O (5 mL) and was extracted with EtOAc (10 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 50:1 to 30:1) to afford **5e** (15.4 mg, 20% yield, colorless oil) and **5ea** (37.1 mg, 40%, colorless oil), respectively.

*Penta-1,4-diene-1,1-diyldibenzene (**5e**).* 15.4 mg (20%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40−7.20 (m, 10H), 6.12 (t, J = 7.6 Hz, 1H), 5.93−5.85 (m, 1H), 5.12−5.03 (m, 2H), 2.87 (dd, J = 7.6, 6.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 142.6, 139.9, 137.0, 129.8, 128.2, 128.1, 127.3, 127.1, 127.0, 126.7, 115.1, 34.1; IR (KBr) υ 2975, 2922, 2359, 1948, 1884, 1809, 1713, 1637, 1597, 1492, 1443, 1360, 1275, 1218, 1156, 1074, 1028, 992, 910, 852, 758 cm^{-1}; HRMS (quadrupole, FAB) calcd for $C_{17}H_{17}$ $[M + H]^+$ 221.1332, found 221.1331.

*(1Z,3E)-1-Phenylpenta-1,3-dienyl Dimethylcarbamate (**5ea**).* 37.1 mg (40%); Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.28−7.22 (m, 1H), 6.41 (d, J = 10.7 Hz, 1H), 6.30−6.24 (m, 1H), 5.89 (dq, J = 13.7, 6.8 Hz, 1H), 3.19 (s, 3H), 2.99 (s, 3H), 1.83 (d, J = 13.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 144.4, 135.6, 131.7, 128.5, 127.9, 124.9, 124.3, 117.3, 36.5, 36.4, 18.7; IR (KBr) υ 2924, 2853, 1716, 1492, 1445, 1489, 1327, 1264, 1151, 1046, 966, 853, 754 cm^{-1}; HRMS (quadrupole, FAB) calcd for $C_{14}H_{18}NO_2$ $[M + H]^+$ 221.1339, found 232.1338.

Experimental Procedure and Characterization Data for the Pd-Catalyzed Hydrogenation of 3a. To an oven-dried sealed tube charged with **3a** (52.3 mg, 0.2 mmol, 100 mol %) in MeOH (2 mL) was added 10% Pd/C (21 mg, 0.02 mmol, 10 mol %). The reaction mixture was stirred under a hydrogen balloon for 3 h at room temperature and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 5:1) to afford **5f** (32.8 mg) in 62% yield as a colorless syrup.

*6-Hydroxy-1-phenylhexyl Dimethylcarbamate (**5f**).* 32.8 mg (62%); Colorless syrup; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34−7.30 (m, 4H), 5.65 (dd, J = 7.6, 6.1 Hz, 1H), 3.60 (t, J = 6.3 Hz, 2H), 2.96 (s, 3H), 2.88 (s, 3H), 1.93−1.90 (m, 1H), 1.78−1.75 (m, 1H), 1.40−1.28 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 141.5, 128.3, 127.5, 126.2, 76.7, 62.6, 36.7, 36.4, 35.8, 32.5, 25.3, 25.1; IR (KBr) υ 3416, 2932, 2858, 2360, 1684, 1493, 1454, 1394, 1186, 1050, 762 cm^{-1}; HRMS (quadrupole, FAB) calcd for $C_{15}H_{24}NO_3$ $[M]^+$ 266.1761, found 266.1758.

Experimental Procedure for the Preparation of Deuterio-1a. To an oven-dried round flask charged with sodium hydride (360 mg, 9.0 mmol, 60% suspension in oil) was added DMSO-d_6 (16 mL) at room temperature. The reaction mixture was stirred for 2 h at 50 °C, and the resulting mixture was cooled to room temperature. To the reaction mixture, a solution of acetophenone-d_3 (0.9 g, 7.5 mmol) in DMSO-d_6 (1.8 mL) was added dropwise in 10 min and further stirred for 20 min at room temperature. To the resulting mixture, a solution of dimethylcarbamoyl chloride (0.83 mL, 9.0 mmol) in DMSO-d_6 (1.8 mL) was added dropwise in 15 min at room temperature. The reaction mixture was stirred for overnight, and quenched with D_2O (20 mL). The mixture was extracted with EtOAc (20 mL × 3). The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 6:1) to afford **deuterio-1a** (434 mg) in 30% yield. ^1H NMR analysis indicated a mixture of three products in the following ratio: d_2-**1a**:(*E*)-d_1-**1a**:(*Z*)-d_1-**1a** = 94:3:3.

Kinetic Isotope Effect (KIE) Experiments. To an oven-dried sealed tube charged with 1-phenylvinyl dimethylcarbamate (**1a**) (38.2 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %), and $Cu(OAc)_2$ (10.8 mg, 0.06 mmol, 30 mol %) were added 4-vinyl-1,3-dioxolan-2-one (**2a**) (45.6 mg, 0.4 mmol, 200 mol %) and *t*-AmOH (1 mL). In another reaction tube, **deuterio-1a** (35.0 mg, 0.2 mmol, 100 mol %) was used as a substrate under otherwise identical conditions. The two reactions were allowed to stir for 45 min at room temperature, reaching around 25% conversion. The two reaction mixtures were diluted with EtOAc (5 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 2:1) to afford **3a** (7.52 mg, 14.4% yield) and **deuterio-3a** (4.7 mg, 9% yield), indicating a KIE value of 1.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02562.

General methods, 1D NOE spectral data of **4f**, and spectroscopic data for all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +82-31-290-7788. Fax: +82-31-292-8800. E-mail: insukim@skku.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIP) (Nos. 2015R1A2A1A15053033, 2015H1D3A1058932, and 2013R1A1A2058800).

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