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Regio- and Stereospecific *C*- and *O*-Allylation of Phenols via π-Allyl Pd Complexes Derived from Allylic Ester Carbonates

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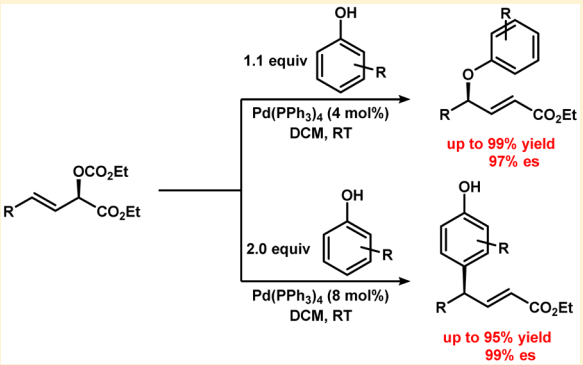
Supporting Information

ABSTRACT: Two complementary strategies have been developed for the *C*- and *O*-allylation of phenols via a common π-allyl Pd complex. While *O*-allylation of phenols by this method is a well-recognized reaction of general utility, the associated *para*-selective *C*-allylation reaction is still in its infancy. Cationic π-allyl Pd intermediates, derived from allylic ester carbonates and palladium(0) catalyst, were found to undergo the Friedel−Crafts-type *para*-selective *C*-allylations with nine different phenols. Both *C*- and *O*-allylated products were obtained in good to excellent yields following a metal-catalyzed regio- and stereospecific substitutive 1,3-transposition. Conditions were also identified that control access to either allylated product. Finally, a study of the equilibrium established between the two allylation products revealed that the *O*-allylated compound was the kinetic product and the *C*-allylated compound the thermodynamic product.



INTRODUCTION

Selective formation of bonds to phenols is an important goal of organic synthesis. For instance, the C−O aryl ether bond is present in many antidepressant drugs, such as Cymbalta ((*S*)-duloxetine) and Prozac (fluoxetine). Carbon−carbon aryl bonds are present in countless natural products. A particularly privileged motif containing C−C aryl bonds is the 1,1-diaryl alkane pattern present in podophyllotoxin and isolariciresinol dimethyl ether from the tetralin family of natural products (Figure 1).[1,2] Accordingly, new methods to construct both types of linkages under mild conditions with excellent regioselectivity and stereospecificity would be useful adjuncts for organic chemists.

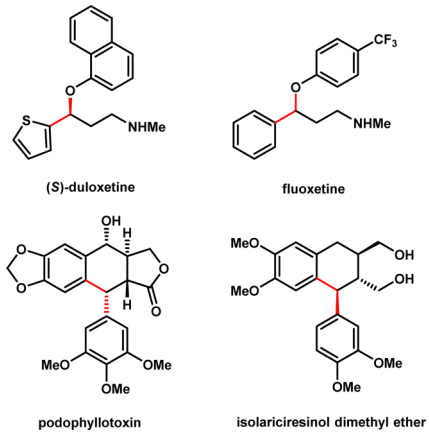


Figure 1. Privileged structures with aryl ether or 1,1-diaryl alkane moieties exhibiting potent biological activity.

Transition-metal-catalyzed transformations have emerged as a powerful method to construct C−C and C−O bonds.[3] Although many strategies utilizing transition metal π-allyl complexes exist to build the aryl ether bond with both regio- and stereoselectivity,[4] relatively few have been reported to accomplish *para*-selective *C*-allylation (Scheme 1).[5−8] Most commonly, *C*-allylation of phenols is achieved in two steps via *O*-allylation followed by an aromatic Claisen rearrangement to forge the C−C bond.[9] Trost reported a strategy to accomplish *O*-allylation of phenols through an asymmetric Pd-catalyzed allylic alkylation and *C*-allylation by a subsequent aromatic Claisen rearrangement.[10] This strategy, however, is limited to *ortho* substitution with respect to the phenol.

Alternatively, the sp^2 aryl and sp^3 allyl moieties can be directly coupled through the π-allyl intermediate. Several processes have been reported to allylate phenols through Friedel−Crafts-type reactivity.[5−8] Kocovsky and Pregosin developed intermolecular transition-metal-catalyzed allylations of arenes through π-allyl species derived from Mo and Ru, respectively.[5,6] Both methods demonstrated high selectivity for substitution at the *para* position of the phenol and the less substituted terminus of the π-allyl. Additionally, enantioselective, intramolecular *C*-allylation of phenols was reported by the Hamada, Wu, and You laboratories.[7,8]

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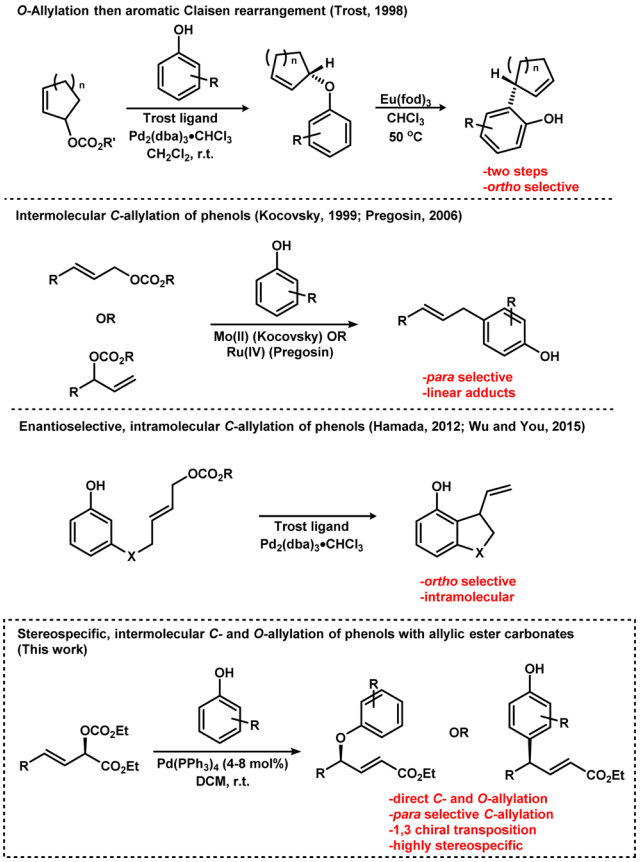
Scheme 1. Strategies to Accomplish C- and O-Allylation of Phenols



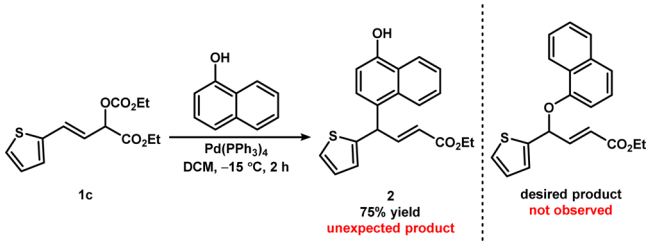
Although the aforementioned methods provide efficient access to either *C*- or *O*-allylated phenols, there lacks a general method to perform intermolecular *O*-allylation and *para*-selective *C*-allylation of phenols with regio- and stereocontrol using the synthetically versatile allylic ester carbonate (**1**) framework. Elegant experiments from the Sinou laboratory suggested that both *C*- and *O*-allylated phenols are in equilibrium with the cationic π-allyl Pd intermediate.[11] Herein, we build upon this notion and report a strategy to manage this equilibrium and effectively direct access to either product. Our group has previously shown that such substitution reactions on these allylic substrates proceed with ample regio- and stereochemical integrity.[12,13]

RESULTS AND DISCUSSION

We initiated investigations into the *C*- and *O*-allylation of phenols following a serendipitous discovery through our ongoing efforts to synthesize the noted antidepressant (*S*)-duloxetine. Our vision was to utilize a π-allyl Pd-mediated substitutive 1,3-chiral transposition to construct the requisite aryl ether bond featured in the target's structure. Surprisingly, when the transformation was attempted with thiophene-substituted allylic ester carbonate **1c** and 1-naphthol, the desired *O*-allylated product was not observed (Scheme 2). Instead, we unexpectedly obtained *C*-allylated product **2** in 75% yield, prompting our exploration into the factors and conditions affecting *C*- versus *O*-allylation of phenols.

Our research inquiry was attentively focused on the three structurally related allylic ester carbonates **1a**–**c**, all suitable substrates for this palladium-catalyzed substitution reaction.

Scheme 2. Reaction between Allylic Ester Carbonate 1c and 1-Naphthol[a]



[a]Reaction run on 0.11 mmol scale with 1.1 equiv of 1-naphthol and 2 mol % $Pd(PPh_3)_4$ in CH_2Cl_2 (0.05 M in carbonate).

With such disparate γ-substituents on **1** (R = methyl, **1a**; phenyl, **1b**; and 2-thienyl, **1c**) paired in reaction with various phenols of diverse substitution pattern, we hoped to interrogate the electronic and steric parameters of the putative π-allyl Pd intermediate in search of insight. Our challenge was to develop a strategy to influence the outcomes of *C*- vs *O*-allylation in the palladium-catalyzed reactions between phenols and allylic carbonates **1**.

Aryl etherification of allylic carbonates **1a**–**c** was achieved in good to excellent yield using 4 mol % of $Pd(PPh_3)_4$ and 1.1 equiv of the phenol at ambient temperature in CH_2Cl_2 (Table 1). As expected, etherification was completely regioselective, affording only regioisomers that corresponded to γ-substitution of the π-allyl Pd intermediate with respect to the ester functionality.[14,15] Notably, 1,3-transpositions were observed exclusively, even with an aromatic substituent at the γ-position of the allylic carbonate (**1b** and **1c**). Apparently, energy-lowering conjugative overlap with the ester carbonyl outcompetes conjugation with the aromatic π system.[16] *O*-Allylation was also efficient with both electron-donating and -withdrawing aromatic substituents.[17,18]

Additionally, aryl etherification was found to be tolerant of phenols with sterically demanding substituents at the 2- and 2,6-positions as underscored by adducts derived from 2,6-diisopropylphenol (**3f**, **4f**) and 2-*tert*-butylphenol (**3g**–**5g**).[19] There were exceptions to the aforementioned model where little or no etherification occurred, but these cases were wholly confined to select phenols reacting with 2-thienyl carbonate **1c**. Four hindered phenols fell into this category: 2,6-diisopropylphenol, methyl salicylate, 2,6-dimethoxyphenol, and 1-naphthol. Both 2,6-diisopropylphenol and methyl salicylate reacted unpredictably with **1c** to form an unwelcomed mix of products that offered little insight and were thus abandoned from further study. In striking contrast, the reaction between 2,6-dimethoxyphenol and carbonate **1c** provided a 52% yield of *C*-allylated adduct **8f** as the sole product (Scheme 3). This result mirrored our earlier (*S*)-duloxetine-inspired finding where exposure of 1-naphthol and **1c** to the palladium(0) catalyst produced exclusively the *C*-allylated product **2**. Equally engrossing was the reaction between **1c** and 2,6-dimethylphenol. At 0 °C, the reaction cleanly afforded aryl ether **5d**, whereas at room temperature the reaction delivered an equilibrating mixture of the *O*- (**5d**) and *C*-allylated (**8e**) adducts in a 34:57 ratio, respectively. These data implied that **5d** was the kinetic product and **8e** the thermodynamic product.

We were intrigued by the dichotomous nature of this reaction and sought to explore the origins of this unusual regioselectivity that leads to *para*-selective *C*-allylation of phenols. We focused our study on reaction optimization and

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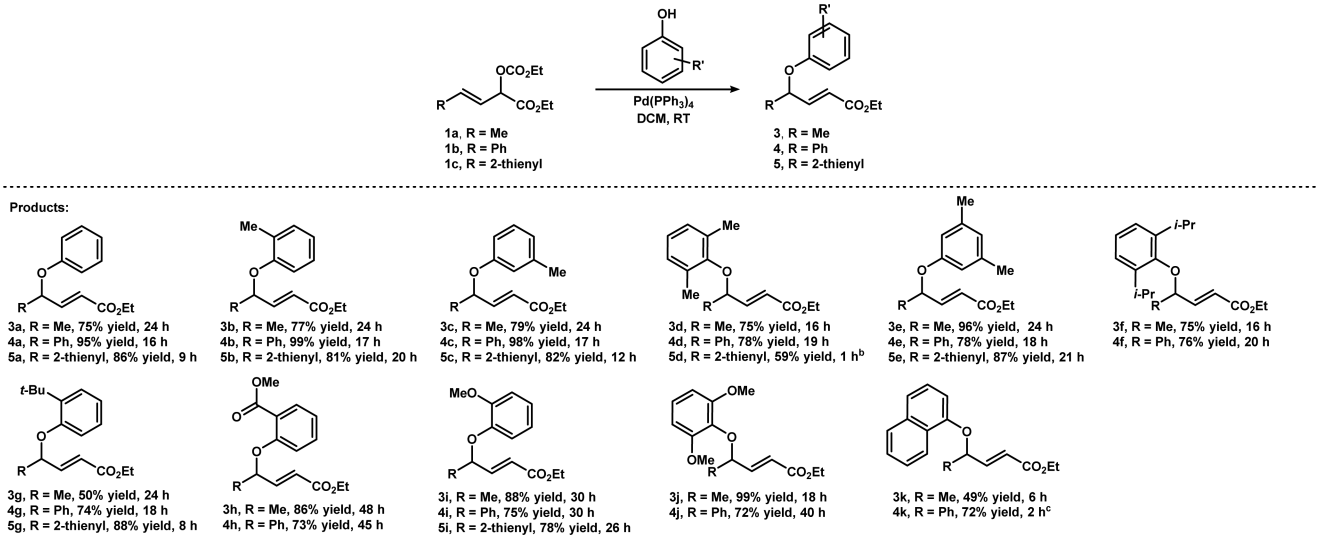
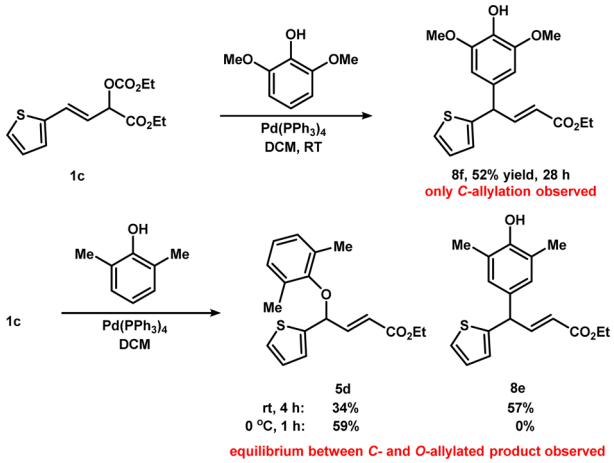
Table 1. Palladium-Catalyzed Aryl Etherification of Allylic Ester Carbonates[a]



[a]Reactions were run on 0.11 mmol scale with 1.1 equiv of phenol and 4 mol % $Pd(PPh_3)_4$ in CH_2Cl_2 (0.05 M in carbonate). [b]Reaction run at 0 °C. [c]Reaction run at −78 °C and warmed to ambient temperature.

Scheme 3. Unique Reactivity of the Thiophene-Substituted Allylic Ester Carbonate 1c[a]



[a]Reactions were run on 0.11 mmol scale with 1.1 equiv of phenol and 4 mol % $Pd(PPh_3)_4$ in CH_2Cl_2 (0.05 M in carbonate).

the determination of scope. The results of this investigation are detailed in Table 2. To our delight, we discovered by simply increasing the catalyst loading to 8 mol %, doubling the concentration of the phenol to 2.0 equiv, and allowing for longer reaction times that the corresponding *C*-allylated products could be obtained in yields that ranged from modest to excellent. These Friedel−Crafts-type allylation reactions were also found to be exceedingly regioselective, proceeding with both high *para* selectivity on the phenol and γ-selectivity on the allylic terminus consistent with 1,3-transposed products.

Substitution patterns on the phenols had a dramatic impact on product outcomes. We found *C*-allylation yields were boosted as the steric bulk at the 2- and 2,6-positions of a substituted phenol increased, presumably due to steric interactions interfering with C−O bond formation. *C*-Allylated adducts derived from phenol (**8a**), 2-methylphenol (**8b**), and 2-*tert*-butylphenol (**8c**) exhibited a predictable trend in reactivity in which the ascending yields of 41%, 59%, and 74%, respectively, were positively correlated with the A-values of their substituents.[20,21] If, however, the methyl group occupies the 3-position on the monosubstituted phenol, the equivalent *C*-allylated product **8d** decreases in yield to 45%. Curiously, although thienyl carbonate **1c** readily formed *C*-allylated products with nine different phenols, carbonates **1a** and **1b** underwent the analogous reaction with just one, 2,6-di-*tert*-butylphenol, to give rise to adducts **6h** (41%) and **7h** (75%), correspondingly. Apparently, only the most-severe sterically congested phenols are potential *C*-allylation substrates for these two carbonates.

The 2,6-disubstituted series of phenols with carbonate **1c** were the best overall performers in the *C*-allylation category. No clear association between structure and yield could be inferred from the data. The highest yields were obtained with adducts derived from 2,6-dimethylphenol (**8e**, 95%) and 2,6-dimethoxyphenol (**8f**, 88%). Surprisingly, when 1-naphthol was subjected to carbonate **1c** under the reaction conditions optimized for *C*-allylation, a complicated blend of products resulted. If, on the other hand, the reaction was conducted at lower temperatures (−15 °C), lower catalyst loadings (2 mol % $Pd(PPh_3)_4$), and lower phenol equivalencies (1.1 equiv), the transformation produced *C*-allylated product **2** in 75% yield.

A cursory investigation into the factors governing C−O and C−C allylic bond formations seemed appropriate at this juncture. The room temperature reaction between carbonate **1c** and 2,6-dimethylphenol was selected as the subject of this study since it had afforded an appealing mix of *O*- (**5d**) and *C*-allylated (**8e**) products. A variety of conditions were investigated, and the results were tabulated in Table 3. Entries 1−4 clearly demonstrate that the triphenylphosphine ligand was crucial to maintaining the efficiency of both the palladium-mediated C−O and C−C allylic bond formations. And while the PCy_3 ligand trial led to diminished yields of **8e**, dppe produced no products at all. The effects of temperature and reaction duration were also examined. As expected, lower temperatures and shorter reaction times favored the kinetic aryl ether product **5d** and higher temperatures and longer reaction times favored the thermodynamic *C*-allylated product **8e**. Interestingly, the solvent THF was shown to singularly favor

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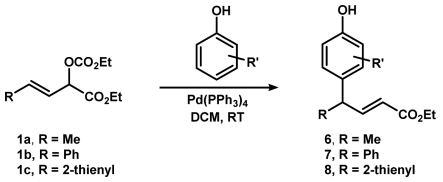
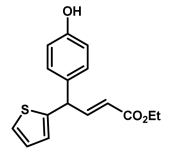
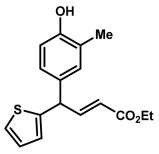
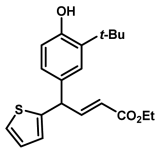
Table 2. Friedel–Crafts-Type *para*-Selective C-Allylation of Phenols[a]

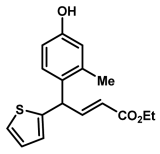


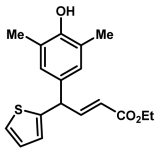
Products:

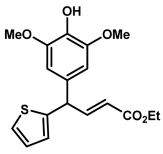

8a, 41% yield, 66 h

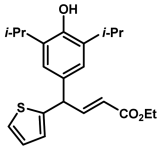

8b, 59% yield, 48 h

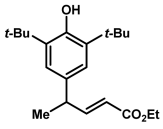

8c, 74% yield, 28 h

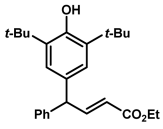

8d, 45% yield, 65 h

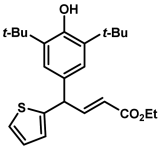

8e, 95% yield, 4 h

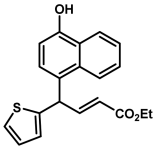

8f, 88% yield, 24 h


8g, 65% yield, 48 h


6h, 41% yield, 24 h

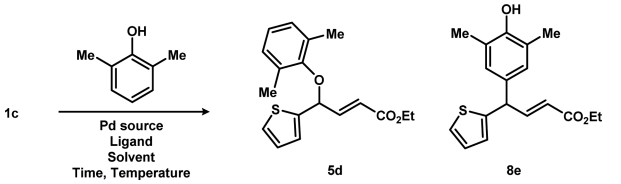

7h, 75% yield, 18 h


8h, 76% yield, 20 h


2, 75% yield, 2 h[b]

[a]Reactions run on 0.11 mmol scale with 2.0 equiv of phenol and 8 mol % $Pd(PPh_3)_4$ in CH_2Cl_2 (0.05 M in carbonate). [b]Reaction run at −15 °C with 2 mol % $Pd(PPh_3)_4$ and 1.1 equiv of phenol.

Table 3. Factors Affecting C–O (5d) and C–C (8e) Allylic Bond Formation[a]



entry	Pd source	ligand	solvent	time	*T*	5d	8e
1	$Pd_2(dba)_3$	PPh_3	DCM	4 h	rt	22	30
2	$Pd_2(dba)_3$	dppe	DCM	4 h	rt	0	0
3	$Pd_2(dba)_3$	PCy_3	DCM	4 h	rt	21	13
4	$Pd(PPh_3)_4$	–	DCM	4 h	rt	34	57
5	$Pd(PPh_3)_4$	–	DCM	1 h	0 °C	59	0
6	$Pd(PPh_3)_4$	–	THF	1 h	rt	26	0
7	$Pd(PPh_3)_4$	–	THF	4 h	rt	40	0

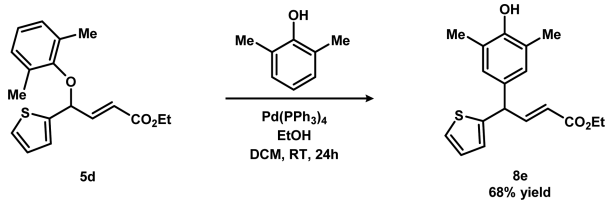
[a]Reactions run on 0.11 mmol scale with 1.1 equiv of phenol, 4 mol % Pd source, and 4 mol % ligand in solvent (0.05 M in carbonate).

C–O allylic bond formation even after 4 h at room temperature (entries 6 and 7).

A straightforward experiment was also devised to support the proposition of a dynamic equilibrium between *O*-allylated product **5d** and *C*-allylated product **8e** (Scheme 4). Pure **5d** was loaded into a flask with 4 mol % of $Pd(PPh_3)_4$ and 2,6-dimethylphenol in DCM. After an extended reaction period of 24 h, *C*-allylated phenol **8e** was isolated from the reaction mixture in 68% yield.[22]

For the purpose of determining relative rate comparisons, a modest ^1H NMR kinetics experiment was performed that monitored the conversion of carbonate **1c** to aryl ether **5d**, and then the consumption and conversion of **5d** to the C-allylated phenol **8e** (Figure 2). In this experiment, carbonate **1c** and 2,6-dimethylphenol were inserted into an NMR tube with $CDCl_3$ and a zero time point ^1H NMR spectrum was taken, signifying

Scheme 4. Pd-Mediated Conversion of *O*-Allylated Product 5d to *C*-Allylated Product 8e[a]



[a]Reaction run on 0.06 mmol scale with 1.0 equiv of 2,6-dimethylphenol, 4 mol % $Pd(PPh_3)_4$, and 1.0 equiv of EtOH in CH_2Cl_2 (0.05 M in aryl ether).

that no reaction had taken place. A $CDCl_3$ solution of $Pd(PPh_3)_4$ was then added to the sample, and ^1H NMR spectra were repeatedly measured in 5 min intervals. The molar ratio of products at each time point was determined by integrating the cleanly separated peaks at 6.1 ppm (dd, J = 15.8, 7.0 Hz, 1H) for **1c**, at 5.5 ppm (dd, J = 5.8, 1.4 Hz, 1H) for **5d**, and at 5.8 ppm (dd, J = 15.5, 1.4 Hz, 1H) for **8e**. The experiment showed that both the consumption of carbonate **1c** and formation of aryl ether **5d** are fast reactions when compared against the relatively slow consumption of **5d** and appearance of **8e**. These data are in accordance with earlier mechanistic speculations that advised that **5d** (C–O formation) is the kinetic product and **8e** (C–C formation) is the thermodynamic product.[23,24]

The stereochemical outcomes of these *C*- and *O*-allylation reactions were of major interest to us. Therefore, we sought facile access to enantioenriched versions of (***R***)-**1b** and (***R***)-**1c** (Scheme 5). As our group has previously shown,[12,13] (*R*)-allylic cyanohydrins are viable precursors to (*R*)-allylic ester carbonates and are readily prepared in excellent yields and enantiomeric excesses through the enantioselective hydrocyanation of *α,β*-unsaturated aldehydes catalyzed by the almond enzyme (*R*)-oxynitrilase.[25] Due to the promiscuity of

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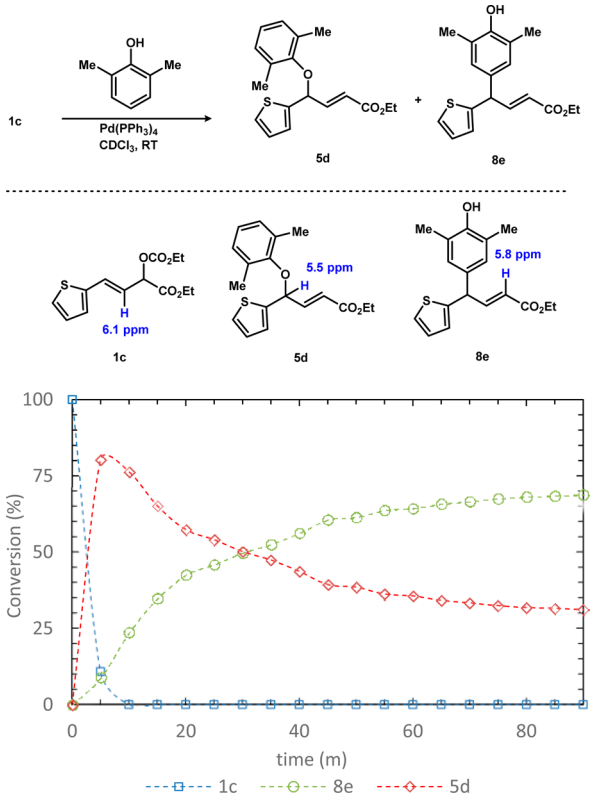
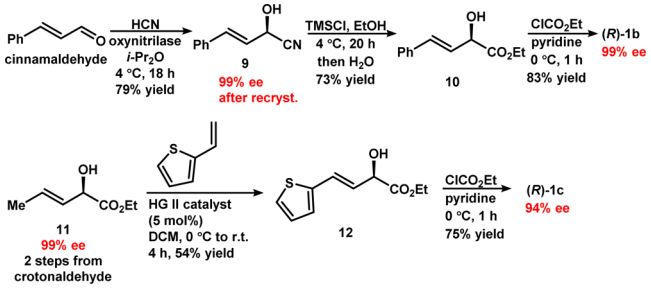


Figure 2. ^{1}H NMR kinetics experiment illustrating the equilibrium between *O*-allylation product **5d** and *C*-allylation product **8e**. Reaction run on 0.05 mmol scale with 3 mol % $Pd(PPh_3)_4$ and 1.1 equiv of 2,6-dimethylphenol in $CDCl_3$ (0.1 M in carbonate).

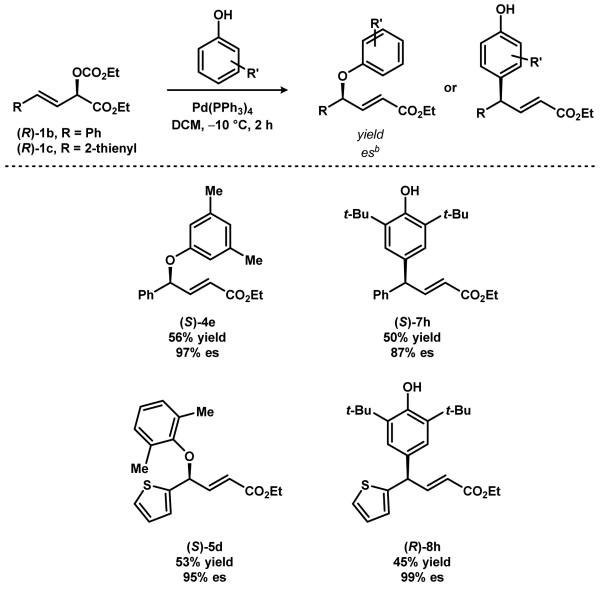
Scheme 5. Preparation of Enantioenriched Allylic Ester Carbonates (*R*)-1b and (*R*)-1c



oxynitrilase [EC 4.1.2.10],[26] the unnatural substrate cinnamaldehyde can be transformed into its corresponding cyanohydrin **9** in 79% yield and 99% ee. Compound **9** was then converted without racemization to α-hydroxy ethyl ester **10** with ethanolic HCl.[27] After ethoxy carbonylation of **10** with ethyl chloroformate in pyridine, phenyl-substituted allylic ester carbonate (*R*)-**1b** was produced in 48% overall yield and 99% ee. The 2-thienyl carbonate (*R*)-**1c** was prepared in two steps from the known α-hydroxy ester **11**.[12] An olefin cross-metathesis reaction using 2-vinyl thiophene and the Hoveyda–Grubbs second generation catalyst furnished the expected 2-thienyl α-hydroxy ester **12**, albeit with a 5% loss in ee.[28−31] This erosion in stereochemistry may be due to Lewis acidic catalyst decomposition products promoting enolization of the labile α-hydroxy ester stereocenter. Following ethoxycarbonylation, carbonate (*R*)-**1c** was isolated in 37% overall yield and 94% ee.

With enantioenriched allylic ester carbonate (*R*)-**1b** and (*R*)-**1c** firmly in hand, we investigated the stereospecificity of the 1,3-transposition reaction fundamental to the *C*- and *O*-allylations of phenols. Well-established precedent has shown that the π-allyl Pd-catalyzed *O*-allylation of phenols proceeds with stereoretention.[11] This result arises from the propensity for soft phenolate nucleophiles to proceed through outer-sphere functionalization, resulting in a double inversion and thus overall retention of stereochemical configuration.[32] Accordingly, the configurational assignments for products **4e**, **5d**, **7h**, and **8h** were founded on the logic of inference, and not of stereochemical correlation.[33,34] By conducting all stereochemical experiments at −10 °C, both *C*- and *O*-allylation products could be generated with good to excellent enantiofidelity (Table 4). Gratifyingly, carbonate (*R*)-**1c** underwent *O*-allylation with 2,6-dimethylphenol and Friedel–Crafts-type *para*-selective *C*-allylation with 2,6-di-*tert*-butylphenol with splendid enantiospecificity at 95% and 99%, respectively. Since these reactions were not optimized, yields were in the moderate range of 53% for (*S*)-**5d** and 45% for (*R*)-**8h**. Similarly, *O*-allylation of the phenyl allylic carbonate ((*R*)-**1b**) with 3,5-dimethylphenol to afford (*S*)-**4e** also proceeded with excellent enantiospecificity (97%) and acceptable yield (56%). Lastly, for the reaction between (*R*)-**1b** and 2,6-di-*tert*-butylphenol, the *C*-allylation product (*S*)-**7h** was obtained in 50% yield with moderate enantiospecificity at 87% es.

Table 4. Stereospecificity of the *C*- and *O*-Allylation Reactions[a]



[a]Reactions run on 0.11 mmol scale with 1.1 equiv of phenol and 4 mol % $Pd(PPh_3)_4$ in CH_2Cl_2 (0.05 M in carbonate). [b]Determined by chiral HPLC, es = enantiospecificity = $(ee_{product})/(ee_{substrate})$.

CONCLUSION

In summary, we have developed a regio- and stereospecific method to accomplish both *C*- and *O*-allylation of phenols via a common chiral π-allyl Pd intermediate. The scope of the *para*-selective *C*-allylation reactions seems to be more limited than the competing *O*-allylation reaction. Significantly, conditions were found that could provide near-exclusive access to either allylation product. Enantioenriched allylic ester carbonates (*R*)-

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1b and (*R*)-**1c** proved to be excellent substrates for the substitutive 1,3-transposition reaction and yielded *C*- and *O*-allylated products with impressive stereofidelity. We also observed a dynamic equilibrium between allylated products **5d** and **8e** and identified the former (C−O−Ar) as the kinetic product and the latter (C−Ar−OH) as the thermodynamic product.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a 300 and 400 MHz spectrometer with $CDCl_3$ as the solvent. Infrared spectra were recorded on an FT-IR spectrometer as a neat liquid on KBr plates. High resolution mass spectra (HRMS) were performed on an electron spray ionization time-of-flight (ESI-TOF) mass spectrometer. Optical rotations were recorded at 589 nm on a polarimeter. Chiral high performance liquid chromatography was performed using a UV detector. Radial chromatography was performed using silica gel coated glass rotors (1, 2, or 4 mm). All nonaqueous reactions were carried out in flame-dried glassware under an argon atmosphere unless otherwise noted. Analytical thin-layer chromatography was performed using 0.25 mm silica gel plates with a fluorescence indicator. α-Hydroxy esters (±)-**10** and (±)-**12** were prepared according to literature procedure.[35,36] Carbonate **1a** and α-hydroxy ester **11** were prepared according to our previously reported procedure.[12]

*(R,E)-2-Hydroxy-4-phenylbut-3-enenitrile (**9**).* Enantioselective hydrocyanation was performed according to our previously reported procedure.[12] KCN (2.9 g, 45.4 mmol) was weighed into a flame-dried flask and dissolved in 20 mL of deionized H_2O. The mixture was sealed and allowed to stir on ice for 5 min. Almond meal was prepared by grinding raw almonds (100 g) to a fine powder, washing 3 times with EtOAc (1.0 L in total), and drying under vacuum (ca. 0.3 mmHg, 12 h) until the almond meal was a dry, free-flowing powder. Almond meal (4.0 g) was added to a 50 mL Erlenmeyer flask and mixed with 3 mL of 20 mM pH 5.5 citrate buffer. The paste was pressed into a thin, even layer against the inside surface of the flask. Cinnamaldehyde (0.95 mL, 7.57 mmol) was added dropwise via syringe evenly onto the surface of the almond meal. This reaction flask was then sealed under a nitrogen atmosphere and chilled on ice. Cold HCl (6 M) was then added to the flask containing the cyanide mixture until a pH of 1 was reached. The solution was transferred to a separatory funnel and extracted (3×) with 40 mL diisopropyl ether. The combined extracts were dried over $MgSO_4$ and then decanted into the previously prepared reaction flask. The solution was stirred at 4 °C for 18 h. The reaction mixture was quenched with the addition of $MgSO_4$ and was then washed through a plug of layered $MgSO_4$ and SiO_2 with anhydrous ether. The solvent was removed under reduced pressure to produce a light yellow solid. The crude solid was recrystallized from CH_2Cl_2 and hexanes to afford 947 mg of **9** as a white crystalline solid in 78.7% yield. ^{1}H and ^{13}C{^{1}H} spectra match those previously reported.[37] R_f = 0.26 (3:1 Hex/EtOAc); $[\alpha]_D^{25}$ = 32.2 (*c*. 0.96, $CHCl_3$) 99% ee.

*Ethyl (R,E)-2-Hydroxy-4-phenylbut-3-enoate (**10**).* Optically pure cyanohydrin **9** (500 mg, 3.14 mmol) was added to a flame-dried, N_2 purged flask and dissolved in 3.14 mL of anhydrous ethanol (1 M). The solution stirred in an ice−water bath for 10 min. Trimethylsilyl chloride (0.783 mL, 6.28 mmol) was added to the reaction mixture dropwise over a 5 min period. The initially colorless reaction turned light brown. After five additional minutes of stirring on ice, the reaction was sealed and moved to a 4 °C cold bath. After 20 h, the reaction mixture was diluted with cold, anhydrous ether and allowed to stir in an ice−water bath for 5 min or until an orange-brown solution almost entirely crystallized. The light brown suspension was filtered through a fine glass frit and washed with cold hexanes and Et_2O. The crystalline solid was transferred to a round-bottom flask, and cold deionized water was added dropwise until the aqueous layer was no longer cloudy. The mixture was transferred to a separatory funnel, and the aqueous phase was extracted (3×) with ether. The combined extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to provide a light yellow oil. The crude residue purified via column chromatography with 3:1 hexanes to ethyl acetate. The crystalline solid was then recrystallized from hexanes to afford 471 mg of **10** as a white crystalline solid in 72.8% yield. ^{1}H and ^{13}C{^{1}H} NMR spectra match those previously reported.[35] R_f = 0.34 (3:1 Hex/EtOAc); $[\alpha]_D^{25}$ = −68.5 (*c*. 1.95, $CHCl_3$) 99% ee.

*Ethyl (R,E)-2-Hydroxy-4-(thiophen-2-yl)but-3-enoate (**12**).* To a flame-dried, N_2 purged flask was added **11** (300 mg, 2.08 mmol) in 1.0 mL of DCM, and the mixture was allowed to stir for 10 min in an ice bath. Hoveyda−Grubbs' second generation catalyst (33 mg, 0.052 mmol) solvated in 1.0 mL of DCM was added. 2-Vinylthiophene (575 mg, 5.20 mmol) in 1.0 mL of DCM was then added dropwise over a period of 5 min, and the reaction was bubbled with N_2 for 1 h. During that time, the reaction changed from a dark green to a brown color. Additional Hoveyda−Grubbs second generation catalyst (33 mg, 0.052 mmol) dissolved in 1.0 mL of DCM was added. After stirring for 3 h at room temperature the reaction was quenched with ethyl vinyl ether, diluted with ether, filtered through $MgSO_4$ and SiO_2, and concentrated under reduced pressure. The crude product was separated via column chromatography (SiO_2, DCM/EtOAc, 20:1) to afford 282 mg of **12** as a pale yellow liquid in 54% yield. Spectral data agree with those reported in literature.[36] R_f = 0.67 (16:1:0.1 DCM/EtOAc/MeOH); $[\alpha]_D^{20}$ = −79.3 (*c*. 1.475, $CHCl_3$); HPLC (Chiracel OD-H) 95:5 Hex/IPA, 0.75 mL/min, t_1 = 10.7 min, t_2 = 12.4 min, 94% ee.

General Procedure for Ethoxy Carbonylation of Allylic α-Hydroxy Esters. α-Hydroxy ester (1 equiv) was weighed into a flame-dried, N_2 purged flask and then dissolved in pyridine (0.5 M). The dissolved mixture was allowed to stir on ice for 90 s. Cold ethyl chloroformate (2.5 equiv) was added dropwise, and the solution was removed from ice and allowed to stir at room temperature. After 45 min, the reaction mixture was diluted with ether and quenched with a saturated solution of NH_4Cl. The reaction mixture was transferred to a separatory funnel and washed with saturated NH_4Cl, 0.1 M HCl, and brine. The aqueous phase was then extracted (3×) with ether. The combined extracts were dried over $MgSO_4$, filtered through SiO_2, and concentrated *in vacuo*. The crude product was then separated via radial chromatography to afford allylic ester carbonate.

*Ethyl (E)-2-((Ethoxycarbonyl)oxy)-4-phenylbut-3-enoate (**1b**).* The general procedure for ethoxy carbonylation of allylic α-hydroxy esters was followed using ethyl (*E*)-2-hydroxy-4-phenylbut-3-enoate (200 mg, 0.97 mmol). The crude product was separated via radial chromatography with 12:1 hexanes to ethyl acetate to afford 224 mg of **1b** as a pale yellow liquid in 83% yield. R_f = 0.4 (7:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.38−7.21 (m, 5H), 6.81 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.9 Hz, 1H), 5.50 (dd, *J* = 7.0, 1.4 Hz, 1H), 4.27−4.17 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$): δ 168.2, 154.1, 135.35, 135.19, 128.52, 128.44, 126.7, 120.2, 75.6, 64.5, 61.8, 14.05, 13.95; IR (KBr, cm^{-1}) ν 2983, 1751, 1280, 1027; HRMS (ESI) calcd for $C_{15}H_{18}O_5Na$ $[M + Na]^+$ 301.1046; found 301.1055.

*Ethyl (R,E)-2-((Ethoxycarbonyl)oxy)-4-phenylbut-3-enoate ((**R**)-**1b**).* The general procedure for ethoxy carbonylation of allylic α-hydroxy esters was followed using **10** (200 mg, 0.97 mmol). The crude product was separated via radial chromatography with 12:1 hexanes to ethyl acetate to afford 224 mg of (*R*)-**1b** as a pale yellow liquid in 83% yield. $[\alpha]_D^{25}$ = −80.1 (*c*. 1.515, $CHCl_3$) 99% ee; HPLC (Chiracel OD-H) 99:1 Hex/IPA, 1 mL/min, t_1 = 7.7 min, t_2 = 8.9 min, 99% ee.

*Ethyl (E)-2-(Ethoxycarbonyloxy)-4-(2-thienyl)-3-butenoate (**1c**).* The general procedure for ethoxy carbonylation of allylic α-hydroxy esters was followed using ethyl (*E*)-2-hydroxy-4-(thiophen-2-yl)but-3-enoate (200 mg, 0.94 mmol). The crude product was separated via radial chromatography (12:1 Hex/EtOAc) to afford 200 mg of **1c** as a pale yellow liquid in 75% yield. R_f = 0.50 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.22 (d, *J* = 5.0 Hz, 1H), 7.04−6.93 (m, 3H), 6.07 (dd, *J* = 15.8, 7.0 Hz, 1H), 5.47 (dd, *J* = 6.9, 1.3 Hz, 1H), 4.31−4.21 (m, 4H), 1.34 (t, *J* = 6.9 Hz, 3H) 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 Hz, $CDCl_3$) δ 168.2, 154.2, 140.4, 128.4, 127.48, 127.40, 125.6, 119.4, 75.4, 64.7, 62.0, 14.16, 14.06; IR (KBr, cm^{-1}) ν 2981, 1745, 1373, 1274, 1247, 1026; HRMS (ESI) calcd for $C_{13}H_{16}O_5S$ $[M]^+$ 284.0718; found 284.0726.

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*Ethyl (R,E)-2-(Ethoxycarbonyloxy)-4-(2-thienyl)-3-butenoate ((R)-**1c**).* The general procedure for ethoxy carbonylation of allylic α-hydroxy esters was followed using **12** (200 mg, 0.94 mmol). The crude product was separated via radial chromatography (12:1 Hex/EtOAc) to afford 200 mg of (***R***)-**1c** as a pale yellow liquid in 75% yield. R_f = 0.50 (3:1 Hex/EtOAc); $[\alpha]_D^{20}$ = −83.9 (*c*. 1.275, $CHCl_3$) 94% ee; HPLC (Chiracel OD-H) 99:1 Hex/IPA, 0.75 mL/min, t_1 = 10.7 min, t_2 = 11.5 min, 94% ee.

General Procedure for Aryl Etherification of Allylic Carbonates. To a stirred solution in a foil-covered vial of phenol (0.12 mmol, 1.1 equiv) and tetrakistriphenylphosphinepalladium(0) (5.1 mg, 0.0044 mmol) in 1.5 mL of dichloromethane was added a solution of carbonate (0.11 mmol, 1 equiv) in 0.7 mL of dichloromethane dropwise at ambient temperature. The reaction progress was monitored by TLC. The reaction was quenched by the addition of Et_2O, filtered through a plug of $MgSO_4$ and SiO_2, concentrated under reduced pressure, and purified by radial chromatography to afford an aryl ether product.

*Ethyl (E)-4-Phenoxypent-2-enoate (**3a**).* The general procedure for aryl etherification was followed using phenol (11.3 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3a** as a pale yellow oil. 18.2 mg, 75% yield. R_f = 0.57 (3:1 Hex/EtOAc). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.61−7.55 (m, 2H), 7.32 (dd, *J* = 15.8, 4.7 Hz, 1H), 7.20−7.17 (m, 3H), 6.35 (dd, *J* = 15.8, 1.6 Hz, 1H), 5.25 (tdd, *J* = 6.5, 4.8, 1.7 Hz, 1H), 4.50 (qd, *J* = 7.1, 0.7 Hz, 2H), 1.79 (d, *J* = 6.6 Hz, 3H), 1.59 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 155.5, 148.3, 130.9, 127.4, 126.6, 120.82, 120.77, 112.6, 72.5, 60.5, 20.7, 16.4, 14.2. IR (KBr, cm^{-1}): ν 2980, 1716, 1597, 1494, 1238, 1176; HRMS (ESI) calcd for $C_{13}H_{16}O_3NH_4$ $[M + NH_4]^+$ 238.1443; found 238.1438.

*Ethyl (E)-4-Phenoxy-4-phenylbut-2-enoate (**4a**).* The general procedure for aryl etherification was followed using phenol (11.3 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4a** as a pale yellow oil, 29.5 mg, 95% yield. R_f = 0.65 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.43−7.22 (m, 7H), 7.12 (dd, *J* = 15.7, 4.9 Hz, 1H), 6.97−6.91 (m, 3H), 6.18 (dd, *J* = 15.7, 1.7 Hz, 1H), 5.78 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 157.4, 146.2, 138.3, 129.4, 128.9, 128.4, 126.7, 121.4, 121.2, 115.9, 78.8, 60.6, 14.2; IR (KBr, cm^{-1}): ν 2981, 1716, 1490, 1276, 1232, 1174, 1031; HRMS (ESI) calcd for $C_{18}H_{18}O_3NH_4$ $[M + NH_4]^+$ 300.1600; found 300.1596.

*Ethyl (E)-4-Phenoxy-4-(thiophen-2-yl)but-2-enoate (**5a**).* The general procedure for aryl etherification was followed using phenol (11.3 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5a** as a pale yellow oil, 27.3 mg, 86% yield. R_f = 0.65 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.34 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.31−7.25 (m, 2H), 7.18 (dd, *J* = 15.6, 5.0 Hz, 1H), 7.10−7.08 (m, 1H), 7.03−6.97 (m, 4H), 6.23 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.05 (dd, *J* = 4.9, 1.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.0, 157.2, 145.1, 141.4, 129.5, 126.9, 126.3, 125.9, 121.96, 121.85, 116.2, 74.8, 60.7, 14.2; IR (KBr, cm^{-1}): ν 2980, 1719, 1659, 1489, 1257, 1157; HRMS (ESI) calcd for $C_{16}H_{16}O_3SNH_4$ $[M + NH_4]^+$ 306.1164; found 306.1157.

*Ethyl (E)-4-(o-Tolyloxy)pent-2-enoate (**3b**).* The general procedure for aryl etherification was followed using *o*-cresol (13.0 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3b** as a pale yellow oil, 19.9 mg, 77% yield. R_f = 0.61 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.16−7.08 (m, 2H), 7.03 (dd, *J* = 15.8, 4.6 Hz, 1H), 6.86 (td, *J* = 7.4, 1.0 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.04 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.94 (qdd, *J* = 6.5, 4.8, 1.6 Hz, 1H), 4.23−4.16 (m, 2H), 2.26 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 155.8, 148.2, 130.8, 127.8, 126.5, 120.7, 112.8, 72.3, 60.6, 21.0, 16.5, 14.4; IR (KBr, cm^{-1}): ν 2924, 2852, 1718, 1490, 1458, 1238; HRMS (ESI) calcd for $C_{14}H_{18}O_3NH_4$ $[M + NH_4]^+$ 252.1600; found 252.1594.

*Ethyl (E)-4-Phenyl-4-(o-tolyloxy)but-2-enoate (**4b**).* The general procedure for aryl etherification was followed using *o*-cresol (13.0 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4b** as a pale yellow oil, 32.3 mg, 99% yield. R_f = 0.74 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44−7.29 (m, 5H), 7.18−7.15 (m, 1H), 7.13 (dd, *J* = 15.6, 4.7 Hz, 1H), 7.07−7.01 (m, 1H), 6.89−6.83 (m, 1H), 6.73 (dd, *J* = 8.0, 0.5 Hz, 1H), 6.22 (dd, *J* = 15.6, 1.7 Hz, 1H), 5.79 (dd, *J* = 4.7, 1.6 Hz, 1H), 4.20 (qd, *J* = 7.1, 0.6 Hz, 2H), 2.35 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 155.3, 146.6, 138.6, 130.8, 128.9, 128.3, 127.4, 126.59, 126.50, 121.0, 120.7, 112.9, 78.5, 60.6, 16.6, 14.2; IR (KBr, cm^{-1}): ν 2981, 2928, 1717, 1492, 1454, 1367, 1301, 1238, 1187, 1121; HRMS (ESI) calcd for $C_{19}H_{20}O_3NH_4$ $[M + NH_4]^+$ 314.1756; found 314.1766.

*Ethyl (E)-4-(Thiophen-2-yl)-4-(o-tolyloxy)but-2-enoate (**5b**).* The general procedure for aryl etherification was followed using *o*-cresol (13.0 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5b** as a pale yellow oil, 27.0 mg, 81% yield. R_f = 0.65 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.32 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.18 (dd, *J* = 15.6, 4.9 Hz, 1H), 7.18−7.10 (m, 2H), 7.07 (ddd, *J* = 3.5, 1.2, 0.7 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.92−6.83 (m, 2H), 6.23 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.06−6.04 (m, 1H), 4.26−4.19 (m, 2H), 2.31 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.0, 155.2, 145.5, 141.8, 131.0, 127.8, 126.8, 126.6, 126.1, 125.6, 121.61, 121.49, 113.3, 74.7, 60.7, 16.5, 14.2; IR (KBr, cm^{-1}): ν 2916, 1751, 1734, 1492, 1234, 1184; HRMS (ESI) calcd for $C_{17}H_{18}O_3SNH_4$ $[M + NH_4]^+$ 320.1320; found 320.1327.

*Ethyl (E)-4-(m-Tolyloxy)pent-2-enoate (**3c**).* The general procedure for aryl etherification was followed using *m*-cresol (13.0 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3c** as a pale yellow oil, 20.4 mg, 79% yield. R_f = 0.58 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.15 (t, *J* = 7.8 Hz, 1H), 7.01 (dd, *J* = 15.8, 4.6 Hz, 1H), 6.78−6.66 (m, 3H), 6.04 (dd, *J* = 15.8, 1.6 Hz, 1H), 4.94 (qdd, *J* = 6.5, 4.8, 1.7 Hz, 1H), 4.23−4.15 (m, 2H), 2.32 (s, 3H), 1.47 (d, *J* = 6.6 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 157.5, 148.0, 139.5, 129.2, 122.0, 121.0, 116.5, 112.4, 72.3, 60.5, 21.5, 20.7, 14.2; IR (KBr, cm^{-1}): ν 2980, 1719, 1659, 1489, 1257, 1157; HRMS (ESI) calcd for $C_{14}H_{18}O_3NH_4$ $[M + NH_4]^+$ 252.1600; found 252.1609.

*Ethyl (E)-4-Phenyl-4-(m-tolyloxy)but-2-enoate (**4c**).* The general procedure for aryl etherification was followed using *m*-cresol (13.0 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4c** as a pale yellow oil, 32.0 mg, 98% yield. R_f = 0.72 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44−7.31 (m, 5H), 7.15−7.09 (m, 2H), 6.78−6.70 (m, 3H), 6.19 (dd, *J* = 15.7, 1.7 Hz, 1H), 5.77 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.30 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 157.4, 146.3, 139.5, 138.4, 129.1, 128.9, 128.3, 126.7, 122.2, 121.1, 116.9, 112.6, 78.6, 60.6, 21.5, 14.2; IR (KBr, cm^{-1}): ν 2980, 1720, 1261, 1193, 1170; HRMS (ESI) calcd for $C_{19}H_{20}O_3NH_4$ $[M + NH_4]^+$ 314.1756; found 314.1754.

*Ethyl (E)-4-(Thiophen-2-yl)-4-(m-tolyloxy)but-2-enoate (**5c**).* The general procedure for aryl etherification was followed using *m*-cresol (13.0 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5c** as a pale yellow oil, 27.3 mg, 82% yield. R_f = 0.65 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.32 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.20−7.12 (m, 2H), 7.07 (ddd, *J* = 3.5, 1.2, 0.7 Hz, 1H), 7.00 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.82−6.75 (m, 3H), 6.21 (dd, *J* = 15.6, 1.6 Hz, 1H), 6.04−6.02 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.0, 157.2, 145.2, 141.5, 139.6, 129.2, 126.9, 126.2, 125.8, 122.7, 121.8, 117.1, 112.8, 74.7, 60.7, 21.4, 14.2; IR (KBr, cm^{-1}): ν 2916, 1751, 1734, 1492, 1234, 1184; HRMS (ESI) calcd for $C_{17}H_{18}O_3SNa$ $[M + Na]^+$ 325.0874; found 325.0874.

*Ethyl (E)-4-(2,6-Dimethylphenoxy)pent-2-enoate (**3d**).* The general procedure for aryl etherification was followed using 2,6-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3d** as a pale yellow oil, 20.5 mg, 75% yield. R_f = 0.60 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.07−6.99 (m, 3H), 6.92 (dd, *J* = 8.5, 6.2 Hz, 1H), 6.02 (dd, *J* = 15.7, 1.4 Hz, 1H), 4.61−4.52 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.25 (d, *J* = 0.2 Hz, 6H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 154.2, 147.9, 131.1, 128.9, 123.7, 121.1, 76.9, 60.5, 20.3, 17.1, 14.2; IR (KBr, cm^{-1}): ν 2976, 2927, 1722, 1475, 1259, 1199, 1047; HRMS (ESI) calcd for $C_{15}H_{20}O_3NH_4$ $[M + NH_4]^+$ 266.1756; found 266.1749.

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*Ethyl (E)-4-(2,6-Dimethylphenoxy)-4-phenylbut-2-enoate (**4d**).* The general procedure for aryl etherification was followed using 2,6-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4d** as a pale yellow oil, 26.6 mg, 78% yield. R_f = 0.74 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.36−7.34 (m, 5H), 7.17 (dd, J = 15.6, 5.9 Hz, 1H), 6.98−6.88 (m, 3H), 6.19 (dd, J = 15.6, 1.5 Hz, 1H), 5.30−5.27 (m, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.05 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 154.6, 146.2, 138.5, 131.2, 128.9, 128.6, 127.8, 123.9, 121.8, 83.3, 60.6, 17.0, 14.2; IR (KBr, cm^{-1}): ν 2980, 1720, 1261, 1193, 1170; HRMS calcd for $C_{20}H_{22}O_3NH_4$ [M + NH_4]$^+$ 328.1913; found 328.1910.

*Ethyl (E)-4-(2,6-Dimethylphenoxy)-4-(thiophen-2-yl)but-2-enoate (**5d**).* The general procedure for aryl etherification was followed, except that the reaction was kept at 0 °C, using 2,6-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5d** as a pale yellow oil, 20.5 mg, 59% yield. R_f = 0.55 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.34 (dd, J = 5.1, 1.2 Hz, 1H), 7.22 (dd, J = 15.6, 5.9 Hz, 1H), 6.99−6.88 (m, 5H), 6.26 (dd, J = 15.5, 1.5 Hz, 1H), 5.56 (dd, J = 5.8, 1.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.08 (s, 6H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 153.9, 144.8, 141.3, 131.4, 128.9, 128.2, 126.87, 126.71, 126.66, 124.2, 122.3, 77.9, 60.6, 16.9, 14.3; IR (KBr, cm^{-1}): ν 2980, 1720, 1300, 1261, 1192, 1176; HRMS (ESI) calcd for $C_{18}H_{20}O_3SH$ [M + H]$^+$ 317.1212; found 317.1197.

*Ethyl (E)-4-(3,5-Dimethylphenoxy)pent-2-enoate (**3e**).* The general procedure for aryl etherification was followed using 3,5-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3e** as a pale yellow oil, 26.2 mg, 96% yield. R_f = 0.59 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.01 (dd, J = 15.8, 4.5 Hz, 1H), 6.61 (s, 1H), 6.51 (s, 2H), 6.04 (dd, J = 15.8, 1.6 Hz, 1H), 4.97−4.89 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.28 (s, 6H), 1.46 (d, J = 6.6 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 157.4, 148.1, 139.1, 122.9, 120.8, 113.3, 72.3, 60.5, 21.4, 20.7, 14.2; IR (KBr, cm^{-1}): ν 2978, 2924, 1718, 1593, 1465, 1294, 1155; HRMS (ESI) calcd for $C_{15}H_{20}O_3H$ [M + H]$^+$ 249.1491; found 249.1502.

*Ethyl (E)-4-(3,5-Dimethylphenoxy)-4-phenylbut-2-enoate (**4e**).* The general procedure for aryl etherification was followed using 3,5-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4e** as a pale yellow oil, 26.6 mg, 78% yield. R_f = 0.74 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.43−7.29 (m, 5H), 7.11 (dd, J = 15.6, 4.8 Hz, 1H), 6.60−6.57 (m, 3H), 6.18 (dd, J = 15.6, 1.7 Hz, 1H), 5.76 (dd, J = 4.8, 1.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.25 (d, J = 0.6 Hz, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 157.4, 146.4, 139.2, 138.5, 128.8, 128.2, 126.7, 123.1, 120.9, 113.6, 78.6, 60.6, 21.4, 14.2; IR (KBr, cm^{-1}): ν 2980, 2926, 1720, 1261, 1193, 1170; HRMS (ESI) calcd for $C_{20}H_{22}O_3H$ [M + H]$^+$ 311.1647; found 311.1653.

*Ethyl (E)-4-(3,5-Dimethylphenoxy)-4-(thiophen-2-yl)but-2-enoate (**5e**).* The general procedure for aryl etherification was followed using 3,5-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5e** as a pale yellow oil, 30.3 mg, 87% yield. R_f = 0.60 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.32 (dd, J = 5.0, 0.9 Hz, 1H), 7.16 (dd, J = 15.6, 4.9 Hz, 1H), 7.07−6.98 (m, 2H), 6.61 (d, J = 9.8 Hz, 3H), 6.20 (dd, J = 15.6, 1.6 Hz, 1H), 6.02 (d, J = 4.2 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 2.27 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.0, 157.2, 145.3, 141.6, 139.2, 126.8, 126.1, 125.6, 123.5, 121.7, 113.7, 74.7, 60.7, 21.5, 14.3; IR (KBr, cm^{-1}): ν 2922, 1722, 1593, 1290, 1151; HRMS (ESI) calcd for $C_{18}H_{20}O_3SH$ [M + H]$^+$ 317.1212; found 317.1221.

*Ethyl (E)-4-(2,6-Diisopropylphenoxy)pent-2-enoate (**3f**).* The general procedure for aryl etherification was followed using 2,6-diisopropylphenol (21.4 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3f** as a pale yellow oil, 25.1 mg, 75% yield. R_f = 0.62 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.04 (dd, J = 15.7, 6.2 Hz, 4H), 5.97 (dd, J = 15.7, 1.2 Hz, 1H), 4.46 (quintetd, J = 6.4, 1.1 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.28 (7, J = 6.9 Hz, 2H), 1.43 (d, J = 6.5 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.19 (dd, J = 6.9, 5.1 Hz, 12H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 150.9, 147.9, 142.0, 124.6, 124.0, 121.5, 78.7, 60.6, 26.7, 24.0, 20.2, 14.2; IR (KBr, cm^{-1}): ν 2964, 2929, 2868, 1722, 1660, 1442, 1257, 1182, 1049; HRMS (ESI) calcd for $C_{19}H_{28}O_3NH_4$ [M + NH_4]$^+$ 322.2382; found 322.2378.

*Ethyl (E)-4-(2,6-Diisopropylphenoxy)-4-phenylbut-2-enoate (**4f**).* The general procedure for aryl etherification was followed using 2,6-diisopropylphenol (21.4 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4f** as a pale yellow oil, 30.6 mg, 76% yield. R_f = 0.60 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.36−7.29 (m, 5H), 7.15 (dd, J = 15.6, 6.3 Hz, 1H), 7.10−7.03 (m, 3H), 6.10 (dd, J = 15.6, 1.4 Hz, 1H), 5.19 (dd, J = 6.3, 1.4 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.12 (7, J = 6.9 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.14 (d, J = 6.9 Hz, 6H), 0.98 (d, J = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.1, 151.4, 146.0, 142.0, 138.3, 128.6, 127.7, 124.7, 124.0, 122.1, 85.2, 60.6, 26.7, 23.90, 23.88, 14.2; IR (KBr, cm^{-1}): ν 2964, 2927, 2868, 1722, 1442, 1298, 1176; HRMS (ESI) calcd for $C_{24}H_{30}O_3NH_4$ [M + NH_4]$^+$ 384.2539; found 384.2543.

*Ethyl (E)-4-(2-(tert-Butyl)phenoxy)pent-2-enoate (**3g**).* The general procedure for aryl etherification was followed using 2-*tert*-butylphenol (18.0 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3g** as a pale yellow oil, 15.2 mg, 50% yield. R_f = 0.58 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.31 (dd, J = 7.7, 1.7 Hz, 1H), 7.15−7.03 (m, 2H), 6.89 (td, J = 7.5, 1.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.01 (dd, J = 15.8, 1.5 Hz, 1H), 5.08−4.99 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.54 (d, J = 6.5 Hz, 3H), 1.42 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 155.9, 148.4, 138.1, 126.9, 121.2, 120.4, 112.8, 72.1, 60.5, 34.8, 29.8, 20.9, 14.2; IR (KBr, cm^{-1}): ν 2954, 2926, 2868, 1722, 1442, 1226; HRMS (ESI) calcd for $C_{17}H_{24}O_3NH_4$ [M + NH_4]$^+$ 294.2069; found 294.2074.

*Ethyl (E)-4-(2-(tert-Butyl)phenoxy)-4-phenylbut-2-enoate (**4g**).* The general procedure for aryl etherification was followed using 2-*tert*-butylphenol (18.0 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4g** as a pale yellow oil, 27.5 mg, 74% yield. R_f = 0.62 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44−7.30 (m, 6H), 7.16 (dd, J = 15.7, 5.1 Hz, 1H), 7.07 (td, J = 7.8, 1.7 Hz, 1H), 6.88 (td, J = 7.5, 1.2 Hz, 1H), 6.74 (dd, J = 8.4, 0.9 Hz, 1H), 6.12 (dd, J = 15.7, 1.5 Hz, 1H), 5.83 (dd, J = 5.1, 1.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.44 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 155.9, 146.4, 138.4, 138.2, 129.0, 128.3, 126.90, 126.87, 121.3, 120.7, 113.3, 79.2, 60.6, 34.9, 29.9, 14.2; IR (KBr, cm^{-1}): ν 2956, 2910, 2868, 1718, 1654, 1442, 1222, 1093; HRMS (ESI) calcd for $C_{22}H_{26}O_3NH_4$ [M + NH_4]$^+$ 356.2226; found 356.2241.

*Ethyl (E)-4-(2-(tert-Butyl)phenoxy)-4-(thiophen-2-yl)but-2-enoate (**5g**).* The general procedure for aryl etherification was followed using 2-*tert*-butylphenol (18.0 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5g** as a pale yellow oil, 33.3 mg, 88% yield. R_f = 0.63 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.34−7.31 (m, 2H), 7.23−7.09 (m, 3H), 7.00 (dd, J = 5.0, 3.5 Hz, 1H), 6.92 (td, J = 7.5, 1.2 Hz, 1H), 6.84 (dd, J = 8.3, 0.8 Hz, 1H), 6.18−6.12 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.42 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.0, 155.6, 145.4, 141.3, 138.4, 127.05, 126.86, 126.3, 125.9, 122.1, 121.0, 113.0, 74.2, 60.8, 34.9, 29.9, 14.2; IR (KBr, cm^{-1}): ν 2956, 1722, 1593, 1219, 1176; HRMS (ESI) calcd for $C_{20}H_{24}O_3SNa$ [M + Na]$^+$ 367.1344; found 367.1335.

*Methyl (E)-2-((5-Ethoxy-5-oxopent-3-en-2-yl)oxy)benzoate (**3h**).* The general procedure for aryl etherification was followed using methyl salicylate (18.3 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3h** as a pale yellow oil, 26.3 mg, 86% yield. R_f = 0.43 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.78 (dd, J = 7.7, 1.8 Hz, 1H), 7.40 (ddd, J = 8.4, 7.4, 1.8 Hz, 1H), 7.04−6.96 (m, 2H), 6.88 (dt, J = 8.4, 0.4 Hz, 1H), 6.13 (dd, J = 15.7, 1.6 Hz, 1H), 5.04−4.95 (m, 1H), 4.18 (qd, J = 7.1, 0.7 Hz, 2H), 3.89 (s, 3H), 1.51 (d, J = 6.5 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.7, 166.2, 156.8, 147.3, 133.2, 131.7, 121.45, 121.38, 120.9, 115.2, 74.0, 60.5, 51.9, 20.4, 14.1; IR (KBr, cm^{-1}): ν 2991, 1719, 1488, 1454, 1248, 1086; HRMS (ESI) calcd for $C_{15}H_{18}O_5H$ [M + H]$^+$ 279.1233; found 279.1234.

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*Methyl (E)-2-((4-Ethoxy-4-oxo-1-phenylbut-2-en-1-yl)oxy)-benzoate (**4h**).* The general procedure for aryl etherification was followed using methyl salicylate (18.3 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4h** as a pale yellow oil, 27.3 mg, 73% yield. R_f = 0.48 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.82 (dd, J = 7.8, 1.6 Hz, 1H), 7.46−7.29 (m, 6H), 7.08 (dd, J = 15.6, 4.6 Hz, 1H), 6.97 (td, J = 7.6, 0.9 Hz, 1H), 6.83 (dt, J = 8.4, 0.5 Hz, 1H), 6.36 (dd, J = 15.6, 1.7 Hz, 1H), 5.85 (dd, J = 4.6, 1.6 Hz, 1H), 4.18 (q, J = 7.0 Hz, 2H), 3.94 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.7, 166.3, 156.5, 145.8, 138.0, 133.2, 131.9, 129.0, 128.4, 126.6, 121.21, 121.09, 121.00, 115.2, 79.5, 60.6, 52.1, 14.2; IR (KBr, cm^{-1}): ν 2981, 1720, 1303, 1246, 1083; HRMS (ESI) calcd for $C_{20}H_{20}O_5NH_4$ [M + NH_4]$^+$ 358.1654; found 358.1638.

*Ethyl (E)-4-(2-Methoxyphenoxy)pent-2-enoate (**3i**).* The general procedure for aryl etherification was followed using 2-methoxyphenol (14.9 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3i** as a pale yellow oil, 24.2 mg, 88% yield. R_f = 0.59 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.06−6.84 (m, 5H), 6.05 (dd, J = 15.8, 1.5 Hz, 1H), 4.92 (qdd, J = 6.6, 5.1, 1.5 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.51 (d, J = 6.6 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 150.3, 148.0, 146.8, 122.2, 121.2, 120.7, 116.6, 112.2, 74.4, 60.4, 55.9, 20.6, 14.2; IR (KBr, cm^{-1}): ν 2980, 1718, 1502, 1253, 1178, 1029; HRMS (ESI) calcd for $C_{14}H_{18}O_4NH_4$ [M + NH_4]$^+$ 268.1549; found 268.1547.

*Ethyl (E)-4-(2-Methoxyphenoxy)-4-phenylbut-2-enoate (**4i**).* The general procedure for aryl etherification was followed using 2-methoxyphenol (14.9 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4i** as a pale yellow oil, 25.8 mg, 75% yield. R_f = 0.54 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.44−7.27 (m, 5H), 7.15 (dd, J = 15.6, 5.3 Hz, 1H), 6.97−6.88 (m, 2H), 6.82−6.74 (m, 2H), 6.18 (dd, J = 15.6, 1.6 Hz, 1H), 5.76 (dd, J = 5.3, 1.5 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 150.5, 146.7, 146.3, 138.5, 128.7, 128.3, 126.9, 122.5, 121.5, 120.7, 117.3, 112.3, 80.4, 60.5, 55.9, 14.2; IR (KBr, cm^{-1}): ν 2980, 1716, 1502, 1454, 1253, 1176; HRMS (ESI) calcd for $C_{19}H_{20}O_4NH_4$ [M + NH_4]$^+$ 330.1705; found 330.1696.

*Ethyl (E)-4-(2-Methoxyphenoxy)-4-(thiophen-2-yl)but-2-enoate (**5i**).* The general procedure for aryl etherification was followed using 2-methoxyphenol (14.9 mg, 0.12 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **5i** as a pale yellow oil, 27.3 mg, 78% yield. R_f = 0.56 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.31 (dd, J = 5.0, 1.3 Hz, 1H), 7.20 (dd, J = 15.6, 5.4 Hz, 1H), 7.03−6.95 (m, 3H), 6.92−6.88 (m, 2H), 6.81 (ddd, J = 8.0, 7.1, 1.7 Hz, 1H), 6.22 (dd, J = 15.6, 1.5 Hz, 1H), 6.01 (ddd, J = 5.4, 1.4, 0.5 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.1, 151.0, 146.3, 145.3, 141.5, 126.7, 126.34, 126.16, 123.4, 122.2, 120.7, 119.2, 112.4, 76.5, 60.6, 55.9, 14.2; IR (KBr, cm^{-1}): ν 2978, 1714, 1514, 1174, 1033; HRMS (ESI) calcd for $C_{17}H_{18}O_4SNa$ [M + Na]$^+$ 341.0823; found 341.0826.

*Ethyl (E)-4-(2,6-Dimethoxyphenoxy)pent-2-enoate (**3j**).* The general procedure for aryl etherification was followed using 2,6-dimethoxyphenol (18.5 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3j** as a pale yellow oil, 30.5 mg, 99% yield. R_f = 0.55 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.06 (dd, J = 15.8, 6.3 Hz, 1H), 6.98 (t, J = 8.4 Hz, 1H), 6.55 (d, J = 8.4 Hz, 2H), 5.95 (dd, J = 15.7, 1.3 Hz, 1H), 4.76 (quintetd, J = 6.5, 1.3 Hz, 1H), 4.16 (qd, J = 7.1, 0.6 Hz, 2H), 3.81 (s, 6H), 1.44 (d, J = 6.6 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.4, 153.7, 148.7, 135.4, 123.9, 120.9, 105.1, 77.4, 60.2, 55.9, 20.4, 14.2; IR (KBr, cm^{-1}): ν 2978, 1716, 1477, 1253, 1111; HRMS (ESI) calcd for $C_{15}H_{20}O_5NH_4$ [M + NH_4]$^+$ 298.1654; found 298.1663.

*Ethyl (E)-4-(2,6-Dimethoxyphenoxy)-4-phenylbut-2-enoate (**4j**).* The general procedure for aryl etherification was followed using 2,6-dimethoxyphenol (18.5 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4j** as a pale yellow oil, 27.1 mg, 72% yield. R_f = 0.49 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.45 (dd, J = 7.9, 1.6 Hz, 2H), 7.35−7.27 (m, 3H), 7.20 (dd, J = 15.7, 6.6 Hz, 1H), 6.95 (t, J = 8.4 Hz, 1H), 6.51 (d, J = 8.4 Hz, 2H), 6.08 (dd, J = 15.7, 1.4 Hz, 1H), 5.72 (dd, J = 6.5, 1.3 Hz, 1H), 4.22−4.11 (m, 2H), 3.76 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.3, 153.6, 146.8, 138.9, 135.1, 128.19, 128.15, 127.6, 124.0, 121.9, 105.2, 82.7, 60.3, 55.9, 14.2; IR (KBr, cm^{-1}): ν 1976, 1716, 1477, 1253, 1111; HRMS (ESI) calcd for $C_{20}H_{22}O_5NH_4$ [M + NH_4]$^+$ 360.1811; found 360.1808.

*Ethyl (E)-4-(Naphthalen-1-yloxy)pent-2-enoate (**3k**).* The general procedure for aryl etherification was followed using 1-naphthol (17.3 mg, 0.12 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **3k** as a pale yellow oil, 14.6 mg, 49% yield. R_f = 0.54 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.35−8.32 (m, 1H), 7.82 (dt, J = 4.6, 2.4 Hz, 1H), 7.54−7.44 (m, 3H), 7.35 (t, J = 7.9 Hz, 1H), 7.12 (dd, J = 15.8, 4.6 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 6.14 (dd, J = 15.8, 1.6 Hz, 1H), 5.17 (qdd, J = 6.4, 4.8, 1.6 Hz, 1H), 4.26−4.15 (m, 2H), 1.62 (d, J = 6.5 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 153.0, 147.8, 134.6, 127.4, 126.4, 125.9, 125.6, 125.3, 122.0, 121.0, 120.6, 106.4, 72.7, 60.5, 20.7, 14.2; IR (KBr, cm^{-1}): ν 2978, 1718, 1577, 1265, 1097; HRMS (ESI) calcd for $C_{17}H_{18}O_3NH_4$ [M + NH_4]$^+$ 288.1600; found 288.1603.

*Ethyl (E)-4-(Naphthalen-1-yloxy)-4-phenylbut-2-enoate (**4k**).* The general procedure for aryl etherification was followed, except for the addition of carbonate, which was performed at −78 °C and then allowed to warm to ambient temperature, using 1-naphthol (17.3 mg, 0.12 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **4k** as a pale yellow oil, 26.3 mg, 72% yield. R_f = 0.75 (100% CH_2Cl_2); ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.44−8.40 (m, 1H), 7.82−7.79 (m, 1H), 7.56−7.29 (m, 8H), 7.27−7.19 (m, 2H), 6.74 (d, J = 7.5 Hz, 1H), 6.29 (dd, J = 15.7, 1.7 Hz, 1H), 6.00 (dd, J = 4.8, 1.5 Hz, 1H), 4.21 (qd, J = 7.1, 0.6 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 152.8, 146.2, 138.3, 134.6, 129.0, 128.4, 127.5, 126.59, 126.48, 125.9, 125.58, 125.44, 122.0, 121.11, 120.94, 107.1, 78.8, 60.7, 14.2; IR (KBr, cm^{-1}): ν 2980, 1718, 1577, 1265, 1174; HRMS (ESI) calcd for $C_{22}H_{20}O_3H$ [M + H]$^+$ 333.1491; found 333.1487.

General Procedure for Allylic Arylation of Allylic Carbonates 1. To a stirred solution in a foil-covered vial of phenol (0.22 mmol, 2.0 equiv) and tetrakistriphenylphosphinepalladium(0) (5.1 mg, 0.0044 mmol) in 1.5 mL of CH_2Cl_2 was added carbonate (0.11 mmol, 1 equiv) in 0.7 mL of CH_2Cl_2 dropwise. An additional 4 mol % of tetrakistriphenylphosphinepalladium(0) (4.9 mg, 0.0042 mmol) in 0.25 mL of CH_2Cl_2 was added after reaction progress had ceased. Progress of reaction was monitored by TLC. The reaction was quenched by the addition of Et_2O, filtered through a plug of $MgSO_4$ and SiO_2, concentrated under reduced pressure, and purified by radial chromatography to afford an allylic phenol product.

*Ethyl (E)-4-(4-Hydroxyphenyl)-4-(thiophen-2-yl)but-2-enoate (**8a**).* The general procedure for allylic arylation was followed using phenol (20.7 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8a** as a pale yellow oil, 13.0 mg, 41% yield. R_f = 0.18 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.33 (dd, J = 15.5, 7.3 Hz, 1H), 7.21 (dd, J = 5.1, 1.2 Hz, 1H), 7.12−7.07 (m, 2H), 6.95 (dd, J = 5.1, 3.5 Hz, 1H), 6.82−6.77 (m, 3H), 5.80 (dd, J = 15.5, 1.4 Hz, 1H), 5.08 (s, 1H), 4.99 (d, J = 7.3 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.6, 154.9, 149.3, 145.3, 133.3, 129.5, 126.9, 125.4, 124.8, 122.3, 115.6, 60.6, 48.0, 14.2; IR (KBr, cm^{-1}): ν 3420, 2878, 1698, 1501, 1180; HRMS (ESI) calcd for $C_{16}H_{16}O_3SNH_4$ [M + NH_4]$^+$ 306.1164; found 306.1174.

*Ethyl (E)-4-(4-Hydroxy-3-methylphenyl)-4-(thiophen-2-yl)but-2-enoate (**8b**).* The general procedure for allylic arylation was followed using *o*-cresol (23.8 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8b** as a pale yellow oil, 19.6 mg, 59% yield. R_f = 0.19 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.33 (dd, J = 15.5, 7.3 Hz, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 6.99−6.91 (m, 3H), 6.80 (dt, J = 3.5, 1.1 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.81 (dd, J = 15.5, 1.4 Hz, 1H), 5.11 (s, 1H), 4.95 (d, J = 7.3 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.22 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.7, 153.2, 149.5, 145.5, 133.1, 130.8, 126.81, 126.75, 125.3, 124.7, 124.2, 122.2, 115.1, 60.6, 48.0, 15.9, 14.2; IR (KBr, cm^{-1}): ν 3423, 2978, 1695, 1508, 1269, 1178; HRMS (ESI) calcd for $C_{17}H_{18}O_3SNa$ [M + Na]$^+$ 325.0874; found 325.0884.

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*Ethyl (E)-4-(3-(tert-Butyl)-4-hydroxyphenyl)-4-(thiophen-2-yl)but-2-enoate (**8c**).* The general procedure for allylic arylation was followed using 2-*tert*-butylphenol (33.0 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8c** as a pale yellow oil, 28.0 mg, 74% yield. R_f = 0.23 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.35 (dd, J = 15.5, 7.5 Hz, 1H), 7.20 (dt, J = 5.1, 0.6 Hz, 1H), 7.12 (d, J = 2.1 Hz, 1H), 6.93 (ddd, J = 13.8, 6.6, 2.9 Hz, 2H), 6.80 (d, J = 3.5 Hz, 1H), 6.64 (d, J = 8.1 Hz, 1H), 5.84 (dd, J = 15.3, 1.2 Hz, 1H), 5.66 (s, 1H), 4.97 (d, J = 7.3 Hz, 1H), 4.21 (q, J = 7.1 Hz, 2H), 1.38 (s, 9H), 1.31−1.27 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz; $CDCl_3$): δ 166.6, 153.4, 149.6, 145.6, 136.4, 132.9, 127.3, 126.8, 126.5, 125.4, 124.6, 122.0, 116.7, 60.5, 48.5, 34.6, 29.5, 14.2; IR (KBr, cm^{-1}): ν 3430, 2962, 1711, 1507, 1170; HRMS (ESI) calcd for $C_{20}H_{24}O_3SNa$ [M + Na]$^+$ 367.1344; found 367.1330.

*Ethyl (E)-4-(4-Hydroxy-2-methylphenyl)-4-(thiophen-2-yl)but-2-enoate (**8d**).* The general procedure for allylic arylation was followed using *m*-cresol (23.8 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8d** as a pale yellow oil, 15.0 mg, 45% yield. R_f = 0.19 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.35 (dd, J = 15.6, 6.4 Hz, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 7.01−6.93 (m, 2H), 6.75 (dt, J = 3.5, 1.1 Hz, 1H), 6.68−6.63 (m, 2H), 5.73 (dd, J = 15.6, 1.7 Hz, 1H), 5.39 (s, 1H), 5.16 (d, J = 6.4 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.8, 154.8, 149.7, 144.8, 137.7, 131.5, 129.3, 126.8, 125.7, 124.7, 122.4, 117.6, 113.0, 60.6, 44.2, 19.6, 14.2; IR (KBr, cm^{-1}): ν 3416, 2878, 1698, 1501, 1178; HRMS (ESI) calcd for $C_{17}H_{18}O_3SNa$ [M + Na]$^+$ 325.0874; found 325.0876.

*Ethyl (E)-4-(4-Hydroxy-3,5-dimethylphenyl)-4-(thiophen-2-yl)but-2-enoate (**8e**).* The general procedure for allylic arylation was followed using 2,6-dimethylphenol (26.8 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8e** as a pale yellow oil, 33.1 mg, 95% yield. R_f = 0.22 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.33 (dd, J = 15.5, 7.4 Hz, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 6.96 (dd, J = 5.1, 3.5 Hz, 1H), 6.85−6.80 (m, 3H), 5.81 (dd, J = 15.5, 1.4 Hz, 1H), 4.92 (d, J = 7.4 Hz, 1H), 4.78 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.22 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.6, 151.5, 149.5, 145.6, 132.6, 128.3, 126.8, 125.2, 124.6, 123.4, 122.1, 60.5, 48.1, 16.0, 14.2; IR (KBr, cm^{-1}): ν 3469, 2978, 1703, 1487, 1199; HRMS (ESI) calcd for $C_{18}H_{20}O_3SNa$ [M + Na]$^+$ 339.1031; found 339.1035.

*Ethyl (E)-4-(4-Hydroxy-3,5-dimethoxyphenyl)-4-(thiophen-2-yl)-but-2-enoate (**8f**).* The general procedure for allylic arylation was followed using 2,6-dimethoxyphenol (33.9 mg, 0.22 mmol) and carbonate **3** (31.3 mg, 0.11 mmol) to afford **8f** as a pale yellow oil, 33.7 mg, 88% yield. R_f = 0.17 (3:1 Hex/EtOAc). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.32 (dd, J = 15.5, 7.3 Hz, 1H), 7.22 (dd, J = 5.1, 1.1 Hz, 1H), 6.96 (dd, J = 5.1, 3.5 Hz, 1H), 6.82 (dt, J = 2.4, 1.1 Hz, 1H), 6.46 (s, 2H), 5.82 (dd, J = 15.5, 1.3 Hz, 1H), 5.51 (s, 1H), 4.96 (d, J = 7.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.84 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.4, 148.9, 147.1, 145.0, 134.0, 132.1, 126.8, 125.4, 124.8, 122.4, 105.0, 60.5, 56.3, 48.9, 14.2; IR (KBr, cm^{-1}): ν 3442, 2918, 1716, 1516, 1215, 1112; HRMS (ESI) calcd $C_{18}H_{20}O_5SNa$ [M + Na]$^+$ 371.0929; found 371.0932.

*Ethyl (E)-4-(4-Hydroxy-3,5-diisopropylphenyl)-4-(thiophen-2-yl)-but-2-enoate (**8g**).* The general procedure for allylic arylation was followed using 2,6-diisopropylphenol (39.2 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8g** as a pale yellow oil, 26.6 mg, 65% yield. R_f = 0.63 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.34 (dd, J = 15.5, 7.5 Hz, 1H), 7.20 (dd, J = 5.1, 1.2 Hz, 1H), 6.97−6.93 (m, 3H), 6.80 (dt, J = 3.5, 1.1 Hz, 1H), 5.84 (dd, J = 15.5, 1.4 Hz, 1H), 4.97 (d, J = 7.5 Hz, 1H), 4.86 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.16 (dt, J = 13.7, 6.9 Hz, 2H), 1.31−1.23 (m, 15H). ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.6, 149.7, 149.2, 145.8, 134.0, 132.8, 126.7, 125.3, 124.6, 123.4, 121.8, 60.4, 48.8, 27.3, 22.66, 22.63, 14.2; IR (KBr, cm^{-1}): ν 3479, 2962, 1703, 1487, 1199; HRMS (ESI) calcd for $C_{22}H_{28}O_3SNa$ [M + Na]$^+$ 395.1657; found 395.1657.

*Ethyl (E)-4-(3,5-Di-tert-butyl-4-hydroxyphenyl)pent-2-enoate (**6h**).* The general procedure for allylic arylation was followed using 2,6-di-*tert*-butylphenol (45.4 mg, 0.22 mmol) and carbonate **1a** (23.8 mg, 0.11 mmol) to afford **6h** as a pale yellow oil, 15.0 mg, 41% yield. R_f = 0.63 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.10 (dd, J = 15.6, 6.9 Hz, 1H), 6.98 (s, 2H), 5.81 (dd, J = 15.6, 1.5 Hz, 1H), 5.12 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.53 (quintetd, J = 7.0, 1.4 Hz, 1H), 1.43−1.39 (m, 21H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 167.0, 153.6, 152.4, 136.0, 133.8, 123.8, 119.3, 60.2, 42.1, 34.4, 30.3, 20.3, 14.3; IR (KBr, cm^{-1}): ν 3643, 2960, 1712, 1433, 1176; HRMS (ESI) calcd for $C_{21}H_{32}O_3Na$ [M + Na]$^+$ 355.2249; found 355.2253.

*Ethyl (E)-4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-phenylbut-2-enoate (**7h**).* The general procedure for allylic arylation was followed using 2,6-di-*tert*-butylphenol (45.4 mg, 0.22 mmol) and carbonate **1b** (30.6 mg, 0.11 mmol) to afford **7h** as a yellow solid, 32.6 mg, 75% yield, mp = 77−79 °C; R_f = 0.55 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.41 (dd, J = 15.6, 7.5 Hz, 1H), 7.35−7.29 (m, 2H), 7.27−7.18 (m, 3H), 6.96 (s, 2H), 5.75 (dd, J = 15.6, 1.5 Hz, 1H), 5.15 (s, 1H), 4.78 (d, J = 7.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.41 (s, 18H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.7, 152.7, 150.9, 142.0, 136.0, 132.0, 128.59, 128.57, 126.7, 125.2, 122.2, 60.4, 53.6, 34.4, 30.3, 14.3; IR (KBr, cm^{-1}): ν 3635, 2956, 1714, 1435, 1235, 1163; HRMS (ESI) calcd for $C_{26}H_{34}O_3Na$ [M + Na]$^+$ 417.2406; found 417.2396.

*Ethyl (E)-4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-(thiophen-2-yl)-but-2-enoate (**8h**).* The general procedure for allylic arylation was followed using 2,6-di-*tert*-butylphenol (45.4 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **8h** as a yellow solid, 33.5 mg, 76% yield, mp: 97−99 °C; R_f = 0.63 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.33 (dd, J = 15.5, 7.6 Hz, 1H), 7.21 (dd, J = 5.1, 1.2 Hz, 1H), 7.05 (s, 2H), 6.96 (dd, J = 5.1, 3.5 Hz, 1H), 6.82 (dt, J = 3.5, 1.1 Hz, 1H), 5.84 (dd, J = 15.5, 1.4 Hz, 1H), 5.19 (s, 1H), 4.96 (d, J = 7.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.42 (s, 18H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.6, 153.0, 149.8, 145.7, 136.0, 131.6, 126.8, 125.3, 124.8, 124.5, 121.7, 60.4, 49.0, 34.4, 30.2, 14.2; IR (KBr, cm^{-1}): ν 3635, 2958, 1714, 1435, 1236, 1161; HRMS (ESI) calcd for $C_{24}H_{32}O_3SNa$ [M + Na]$^+$ 423.1970; found 423.1969.

*Ethyl (E)-4-(4-Hydroxynaphthalen-1-yl)-4-(thiophen-2-yl)but-2-enoate (**2**).* The general procedure for allylic arylation was followed, except that the reaction was performed at −15 °C with 2 mol % tetrakistriphenylphosphinepalladium(0) (2.5 mg, 0.0023 mmol), using 1-naphthol (31.7 mg, 0.22 mmol) and carbonate **1c** (31.3 mg, 0.11 mmol) to afford **2** as a pale yellow oil, 27.9 mg, 75% yield. R_f = 0.20 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.29−8.26 (m, 1H), 7.91 (dt, J = 7.3, 2.6 Hz, 1H), 7.59−7.44 (m, 3H), 7.19−7.14 (m, 2H), 6.92 (dt, J = 5.1, 3.6 Hz, 1H), 6.82−6.76 (m, 2H), 6.34 (s, 1H), 5.84−5.74 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 167.0, 151.7, 150.1, 144.9, 132.2, 129.0, 126.90, 126.86, 126.15, 126.04, 125.11, 124.98, 124.7, 123.3, 122.87, 122.68, 107.7, 60.7, 44.0, 14.2; IR (KBr, cm^{-1}): ν 3444, 2961, 1705, 1518, 1270, 1190; HRMS (ESI) calcd for $C_{20}H_{18}O_3SNa$ [M + Na]$^+$ 361.0874; found 361.0869.

*Interconversion of Aryl Ether **5d** to Allylic Phenol **8e**.* To a stirred solution in a foil-covered vial of aryl ether **5d** (20 mg, 0.063 mmol, 1 equiv) in 1.0 mL of dichloromethane was added 2,6-dimethylphenol (7.7 mg, 0.063 mmol, 1 equiv) and EtOH (3.4 μL, 0.063 mmol, 1 equiv). The reaction was allowed to stir for 5 min. A solution of tetrakistriphenylphosphinepalladium(0) (2.2 mg, 0.0022 mmol) in 0.25 mL of dichloromethane was then added, and the reaction was monitored by TLC until complete. The reaction was quenched by the addition of Et_2O, filtered through a plug of $MgSO_4$ and SiO_2, concentrated under reduced pressure, and purified by radial chromatography to afford **8e**, 12.0 mg, 60% yield.

*^{1}H NMR Kinetics Experiment with Carbonate **1c** and 2,6-Dimethylphenol.* Carbonate **1c** (14 mg, 0.05 mmol, 1 equiv) and 2,6-dimethylphenol (7.0 mg, 0.058 mmol, 1.1 equiv) in 0.4 mL of $CDCl_3$ were added to a 5 mm NMR tube, and a zero-time point ^{1}H NMR spectrum was taken. Tetrakistriphenylphosphinepalladium(0) (1.7 mg, 0.0015 mmol, 0.03 equiv) in 0.1 mL of $CDCl_3$ was added to the NMR tube. The sample tube was immediately sealed under N_2, and the first ^{1}H NMR experiment was measured 5 min after catalyst addition. Subsequent ^{1}H NMR experiments were performed at 5 min intervals

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until no further change in product ratios was observed. The molar ratio of products at each time point was determined by integrating the baseline separated peaks at 6.1 ppm (dd, J = 15.8, 7.0 Hz, 1H) for **1c**, at 5.5 ppm (dd, J = 5.8, 1.4 Hz, 1H) for **5d**, and at 5.8 ppm (dd, J = 15.5, 1.4 Hz, 1H) for **8e**. The molar ratios were normalized to determine relative concentrations and then plotted against time to generate the graph displayed in Figure 2.

General Procedure for Stereospecific Aryl Etherification and Allylic Arylation. To a stirred solution in a foil-covered vial of phenol (0.12 mmol, 1.1 equiv) and tetrakistriphenylphosphine-palladium(0) (2.2 mg, 0.0022 mmol) in 1.5 mL of dichloromethane was added carbonate (0.11 mmol, 1 equiv) dropwise at −10 °C. An additional 2 mol % of tetrakispalladiumtriphenylphosphine(0) (2.2 mg, 0.0022 mmol) in 0.5 mL of dichloromethane was added after reaction progress had ceased. The reaction progress was monitored by TLC. The reaction was quenched by the addition of Et_2O, filtered through a plug of $MgSO_4$ and SiO_2, concentrated under reduced pressure, and purified by radial chromatography to afford the *C*- or *O*-allylated product. The enantiomeric excess was determined by chiral HPLC.

Ethyl (S,E)-4-(3,5-Dimethylphenoxy)-4-phenylbut-2-enoate ((S)-4e). The general procedure for enantiospecific aryl etherification and allylic arylation was followed using 3,5-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate (***R***)-**1b** (30.6 mg, 0.11 mmol) to afford (***S***)-**4e** as a pale yellow oil, 19.1 mg, 56% yield. R_f = 0.74 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.43−7.29 (m, 5H), 7.11 (dd, J = 15.6, 4.8 Hz, 1H), 6.60−6.57 (m, 3H), 6.18 (dd, J = 15.6, 1.7 Hz, 1H), 5.76 (dd, J = 4.8, 1.7 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.25 (d, J = 0.6 Hz, 6H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 157.4, 146.4, 139.2, 138.5, 128.8, 128.2, 126.7, 123.1, 120.9, 113.6, 78.6, 60.6, 21.4, 14.2; IR (KBr, cm^{-1}): ν 2980, 2926, 1720, 1261, 1193, 1170; HPLC (Chiracel OD-H) 99:1 Hex/IPA, 1 mL/min, t_1 = 4.4 min t_2 = 5.1 min, 97% es; HRMS (ESI) calcd for $C_{20}H_{22}O_3H$ $[M + H]^+$ 311.1647; found 311.1653.

Ethyl (S,E)-4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-phenylbut-2-enoate ((S)-7h). The general procedure for enantiospecific aryl etherification and allylic arylation was followed using 2,6-di-*tert*-butylphenol (45.4 mg, 0.22 mmol) and carbonate (***R***)-**1b** (30.6 mg, 0.11 mmol) to afford (***S***)-**7h** as a yellow solid, 21.7 mg, 50% yield, mp =77−79 °C. R_f = 0.55 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.41 (dd, J = 15.6, 7.5 Hz, 1H), 7.35−7.29 (m, 2H), 7.27−7.18 (m, 3H), 6.96 (s, 2H), 5.75 (dd, J = 15.6, 1.5 Hz, 1H), 5.15 (s, 1H), 4.78 (d, J = 7.5 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.41 (s, 18H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.7, 152.7, 150.9, 142.0, 136.0, 132.0, 128.59, 128.57, 126.7, 125.2, 122.2, 60.4, 53.6, 34.4, 30.3, 14.3; IR (KBr, cm^{-1}): ν 3635, 2956, 1714, 1435, 1235, 1163; HPLC (Chiracel OD-H) 99:1 Hex/IPA, 0.75 mL/min, t_1 = 4.2 min, t_2 = 10.2 min, 87% es; HRMS (ESI) calcd for $C_{26}H_{34}O_3Na$ $[M + Na]^+$ 417.2406; found 417.2396.

Ethyl (S,E)-4-(2,6-Dimethylphenoxy)-4-(thiophen-2-yl)but-2-enoate ((S)-5d). The general procedure for aryl etherification was followed using 2,6-dimethylphenol (14.7 mg, 0.12 mmol) and carbonate (***R***)-**1c** (31.3 mg, 0.11 mmol) to afford (***S***)-**5d** as a pale yellow oil, 18.4 mg, 53% yield. R_f = 0.55 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.34 (dd, J = 5.1, 1.2 Hz, 1H), 7.22 (dd, J = 15.6, 5.9 Hz, 1H), 6.99−6.88 (m, 5H), 6.26 (dd, J = 15.5, 1.5 Hz, 1H), 5.56 (dd, J = 5.8, 1.4 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.08 (s, 6H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.2, 153.9, 144.8, 141.3, 131.4, 128.9, 128.2, 126.87, 126.71, 126.66, 124.2, 122.3, 77.9, 60.6, 16.9, 14.3; IR (KBr, cm^{-1}): ν 2980, 1720, 1300, 1261, 1192, 1176; HPLC (Chiracel OD-H) 95:5 Hex/IPA, 1 mL/min, t_1 = 2.9 min t_2 = 3.8 min, 95% es; HRMS (ESI) calcd for $C_{18}H_{20}O_3SH$ $[M + H]^+$ 317.1212; found 317.1197.

Ethyl (R,E)-4-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-(thiophen-2-yl)but-2-enoate ((R)-8h). The general procedure for allylic arylation was followed using 2,6-di-*tert*-butylphenol (45.4 mg, 0.22 mmol) and carbonate (***R***)-**1c** (31.3 mg, 0.11 mmol) to afford (***R***)-**8h** as a yellow solid, 19.8 mg, 45% yield, mp: 97−99 °C. R_f = 0.63 (3:1 Hex/EtOAc); ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.33 (dd, J = 15.5, 7.6 Hz, 1H), 7.21 (dd, J = 5.1, 1.2 Hz, 1H), 7.05 (s, 2H), 6.96 (dd, J = 5.1, 3.5 Hz, 1H), 6.82 (dt, J = 3.5, 1.1 Hz, 1H), 5.84 (dd, J = 15.5, 1.4 Hz, 1H), 5.19 (s, 1H), 4.96 (d, J = 7.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 1.42 (s, 18H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz; $CDCl_3$): δ 166.6, 153.0, 149.8, 145.7, 136.0, 131.6, 126.8, 125.3, 124.8, 124.5, 121.7, 60.4, 49.0, 34.4, 30.2, 14.2; IR (KBr, cm^{-1}): ν 3635, 2958, 1714, 1435, 1236, 1161; HPLC (Chiracel OD-H) 95:5 Hex/IPA, 1.0 mL/min, t_1 = 3.4 min t_2 = 6.9 min, 99% es; HRMS (ESI) calcd for $C_{24}H_{32}O_3SNa$ $[M + Na]^+$ 423.1970; found 423.1969.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02608.

^{1}H and ^{13}C spectra and HPLC traces (PDF)

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