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Formal α-Allylation of Primary Amines by a Dearomative, Palladium-Catalyzed Umpolung Allylation of *N*-(Aryloxy)imines

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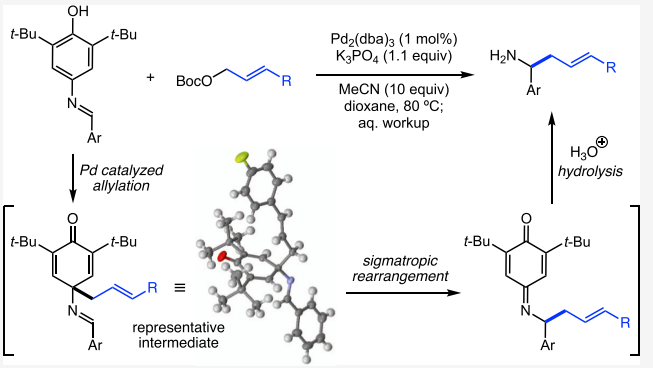
ABSTRACT: *N*-(Aryloxy)imines, readily accessible by condensation/tautomerization of (pseudo)benzylic primary amines and 2,6-di-*tert*-butyl-1,4-benzoquinone, undergo efficient allylation to afford a wide range of homoallylic primary amines following hydrolytic workup. Deprotonation of *N*-(aryloxy)imines generates a delocalized 2-azaallyl anion-type nucleophile that engages in dearomative C−C bond-forming reactions with allylpalladium(II) electrophiles generated from allylic *tert*-butyl carbonates. This reactivity umpolung enables the formal α-allylation of (pseudo)benzylic primary amines. Mechanistic studies reveal that the apparent regioselectivity of the desired bond-forming event is a convergent process that is initiated by unselective allylation of *N*-(aryloxy)-imines to give several regioisomeric species, which subsequently rearrange via stepwise [1,3]- or concerted [3,3]-sigmatropic shifts, ultimately converging to provide the desired regioisomer of the amine products.



INTRODUCTION

Amines are key constituents of naturally occurring molecules of varying complexity and are commonly present in pharmaceuticals, agrochemicals, and materials. Owing to their ubiquitous nature and proven utility, synthetic tools for their efficient and rapid preparation and/or modification are in high demand. Classical approaches to amine synthesis rely heavily on C−N bond construction and include N-alkylation,[1] reductive amination,[2] and the addition of carbon nucleophiles to preformed imines.[3] Many modern methods for amine synthesis, including cross-coupling,[4] hydroamination,[5] and C−H amination,[6] also employ C−N bond construction. Alternatively, amine α-C−H bond functionalization is an attractive transform that not only enables the conversion of simple, readily available amines into more complex structures, but also has the potential to facilitate the late-stage functionalization of amine-containing substrates. Emerging methods to enable this type of reactivity have been driven by advances in photoredox catalysis,[7] dehydrogenative cross-coupling,[8] and amine oxidation chemistry.[9] These new methods for amine α-functionalization commonly rely on the generation of an electron-deficient species (e.g., imine, or iminium) whose native reactivity facilitates coupling with various nucleophilic coupling partners or α-amino radicals that react with radical acceptors.

Our group has recently reported protocols for the stepwise α-C−H functionalization of amines (**2**)[9c] as well as α-C−C functionalization of α-amino acids[9d] and 1,2-amino alcohols[9e] (Scheme 1, C−H functionalization chemistry is highlighted in eq 1). Common to these formal quinone-catalyzed C−H or C−C bond functionalizations is the formation of an *N*-(aryloxy)imine (**3**, Scheme 1), which functions as an electrophile that undergoes transimination with anisidine to provide *N*-para-methoxyphenyl imine **4**, an intermediate that is engaged in a subsequent nucleophilic addition to provide the α-functionalized secondary amine products (**5**). In an effort to develop methods for direct amine α-functionalization, we have explored the possibility of engaging catalytically generated *N*-(aryloxy)imine **3** in direct reactions with various nucleophilic reaction partners (not shown); however, these efforts have not yet been successful. We hypothesized that this lack of success might be in part related to the relatively electron-rich nature of imine **3**, which is likely to exist as its conjugate base under the typical reaction conditions that are employed for amine oxidation. This led us to consider the possibility of utilizing *N*-(aryloxy)imine **3** as a nucleophilic coupling partner that might productively engage in dearomative C−C bond-forming reactions with a variety of electrophiles (Scheme 1, eq 2).

The proposed reactivity umpolung would involve the generation of an amino α-carbanion synthon, which typically

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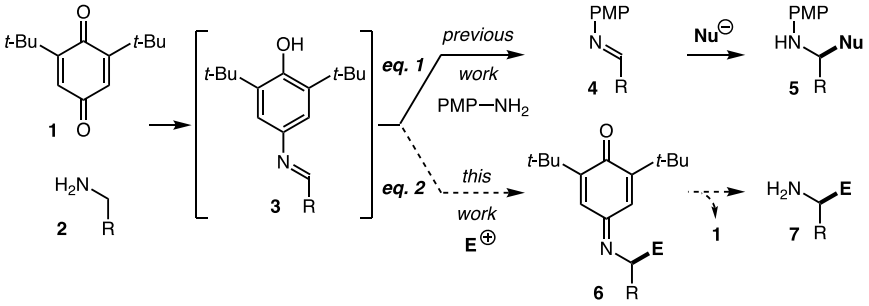
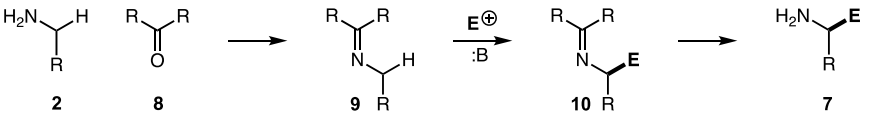
Scheme 1. Previous Quinone-Catalyzed Amine Functionalization Chemistry and Possible Reactivity Umpolung of *N*-(Aryloxy)imine 3

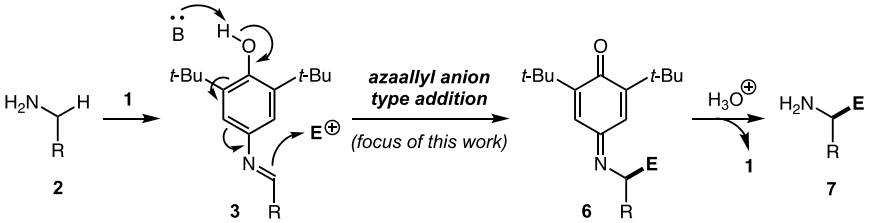


Scheme 2. Classical Azaallyl Anion Chemistry and Proposed Quinone-Mediated α-Functionalization of Amines

Classical Azaallyl Anion Chemistry (eq. 1):



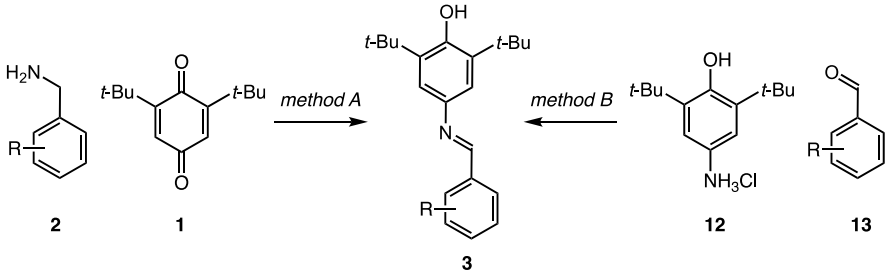
Dearomative Alternative to Classical Azaallyl Anion Chemistry (eq. 2, this work):



Notable features and challenges of the proposed chemistry:

- prior efforts in amine oxidation/functionalization have established methods for the (catalytic) formation of N-(aryloxy)imine **3**
- unprecedented bond-forming event requires loss of aromaticity in N-(aryloxy)imine **3**
- addition of electrophile to N-(aryloxy)imine **3** has the potential to provide a number of undesired regioisomeric products

Scheme 3. Two Methods for the Synthesis of *N*-(Aryloxy)imines (3)



appears in the form of cyanide, nitronate, or 2-azaallyl anions. This nucleophilic synthon provides complementary reactivity when compared to the classical pattern of reactivity associated with amines. The need for subsequent reduction of the nitrile or nitro function has, to some extent limited, the utility of methods that employ cyanide and nitronates. On the other hand, 2-azaallyl anions have received significant attention in recent years, as conversion of the imine products generated in these reactions to the corresponding primary amines is readily accomplished via imine hydrolysis (Scheme 2, eq 1). 2-Azaallyl anions are typically generated by deprotonation of preformed aldimines or ketimines,[10] but they can also be accessed by decarboxylative,[11] reductive,[12] and hydrometallation processes.[13] Additionally, the ability of 2-azaallyl anions to engage in a wide range of reactions with electrophilic coupling partners has led to the successful development of many new reactions of broad utility.[14]

With this framework in mind, we envisioned that deprotonation of *N*-(aryloxy)imine **3**, readily accessible from an amine substrate **2** and quinone **1** by way of condensation, followed by proton transfer (Scheme 2, eq 2), would deliver an azaallyl anion-like nucleophile that could potentially be intercepted by a diverse range of electrophiles (**E**+) to provide iminoquinone **6**. Hydrolysis of **6** would then release the

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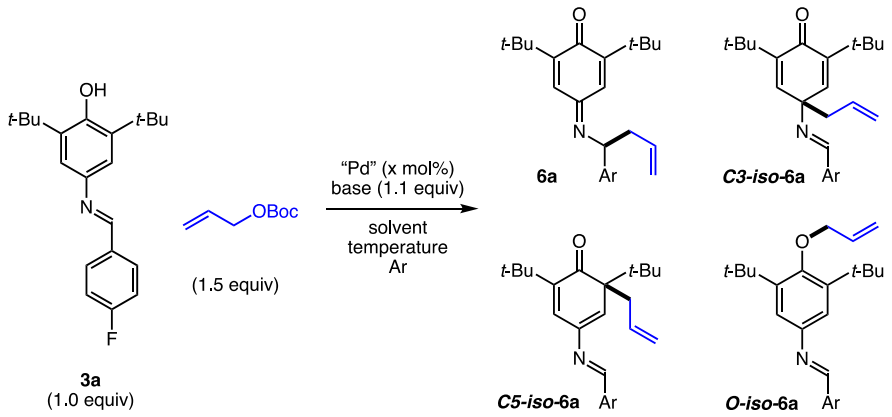
Table 1. Optimization of Reaction Conditions for Dearomative, Pd-Catalyzed Allylation of *N*-(Aryloxy)imine 3a[a]



entry	solvent (s)	base	temp. (°C)	Pd catalyst	yield 6a (%)	yield isomers (%)
1	MeCN	NaOMe	50	$[allylPdCl]_2$ (5 mol %)	17	0
2	MeCN	K_2CO_3	50	$[allylPdCl]_2$ (5 mol %)	76	21
3	MeCN	K_3PO_4	50	$[allylPdCl]_2$ (5 mol %)	70	17
4	MeCN	K_3PO_4	50	$Pd_2(dba)_3$ (5 mol %)	71	13
5	MeCN	K_3PO_4	50	$Pd_2(dba)_3$ (2 mol %)	69	19
6	THF	K_3PO_4	50	$Pd_2(dba)_3$ (2 mol %)	46	17
7	dioxane	K_3PO_4	50	$Pd_2(dba)_3$ (2 mol %)	33	3
8	dioxane/MeCN	K_3PO_4	50	$Pd_2(dba)_3$ (2 mol %)	82	16
9	dioxane/MeCN	K_3PO_4	80	$Pd_2(dba)_3$ (2 mol %)	73	6
10[b]	dioxane	K_3PO_4	50	$Pd_2(dba)_3$ (2 mol %)	76	11
11[b]	dioxane	K_3PO_4	80	$Pd_2(dba)_3$ (2 mol %)	89	9
12[b]	dioxane	K_3PO_4	80	$Pd_2(dba)_3$ (1 mol %)	89	10
13[b,c]	dioxane	K_3PO_4	80		0	0

[a]Yields were determined by ^{1}H nuclear magnetic resonance (NMR) using 1,3,5-trimethoxybenzene as an internal standard. [b]10 equiv of MeCN was used. [c]0% conversion.

functionalized amine product (**7**) and quinone (**1**). While previous work in quinone-catalyzed amine functionalization chemistry has provided ample support for the initial steps of the overall transformation,[9a,c,d,15] we could find no literature precedent to support the proposed bond-forming event, which would require a regioselective, dearomative functionalization of the key *N*-(aryloxy)imine intermediate. Therefore, in an initial effort to establish the feasibility of the proposed chemistry, we chose to study the reaction of preformed *N*-(aryloxy)imines **3** with various electrophilic coupling partners. Herein, we report the discovery of *N*-(aryloxy)imines as useful precursors to 2-azaallyl anion-like species that participate in efficient, dearomative C−C bond-forming reactions. Specifically, we have demonstrated that palladium catalysis unites *N*-(aryloxy)-imines with allyl carbonates to deliver a wide range of homoallylic primary amines.

RESULTS AND DISCUSSION

To facilitate the proposed studies, two methods have been developed to enable the synthesis and isolation of the requisite preformed *N*-(aryloxy)imines (**3**, Scheme 3). In the first method (method A), benzylic amines (**2**) and 2,6-di-*tert*-butyl-1,4-benzoquinone (**1**) were combined and heated to promote condensation and tautomerization, which delivered the corresponding *N*-(aryloxy)imines **3**. These surprisingly stable intermediates were readily purified by recrystallization. In some cases, competitive transimination between the desired product **3** and unreacted amine was observed, thereby leading to the formation of an undesired *N*-benzylic imine as a major side product (not shown) and limiting the efficiency of this process. This side reaction became increasingly problematic with electron-deficient benzylic amines, presumably owing to the increased electrophilicity of the corresponding *N*-(aryloxy)-imines. To circumvent this issue, we used a modified protocol[16] (method B) involving condensation of the corresponding benzaldehyde derivative (**13**) with readily available 4-amino-2,6-di-*tert*-butyl phenol hydrochloride (**12**). Using these methods, we were able to prepare a wide variety of *N*-(aryloxy)imines (**3**) for use in the present study.

We then examined the ability of *N*-(aryloxy)imine **3a** to undergo palladium-catalyzed allylation using allyl *tert*-butyl carbonate (Table 1). We first observed productive allylation when using allyl Pd chloride dimer as a catalyst and sodium methoxide as a base at 50 °C in MeCN (entry 1). This result established that productive bond formation was possible and mitigated our concerns regarding the potential for undesired oxidation of Pd(0) by the iminoquinone product of the reaction (e.g., **6a**)—a process that would likely prevent successful catalysis. We then evaluated a series of bases under these initial reaction conditions. As we had speculated, several regioisomeric products (***C3-iso-6a***, ***C5-iso-6a***, and ***O-iso-6a***) were also observed. Among the bases evaluated (entries 1−3), potassium phosphate provided the best yield of the desired product (**6a**, 82%) while minimizing the formation of the regioisomeric products (combined yield of regioisomers = 12%). The lower yield provided by sodium methoxide is probably because of unproductive consumption of the allylic carbonate or competitive reaction with the allylpalladium electrophile. Using $Pd_2(dba)_3$ as a catalyst led to a comparable yield of **6a** (71%, entry 4) together with only 13% of the

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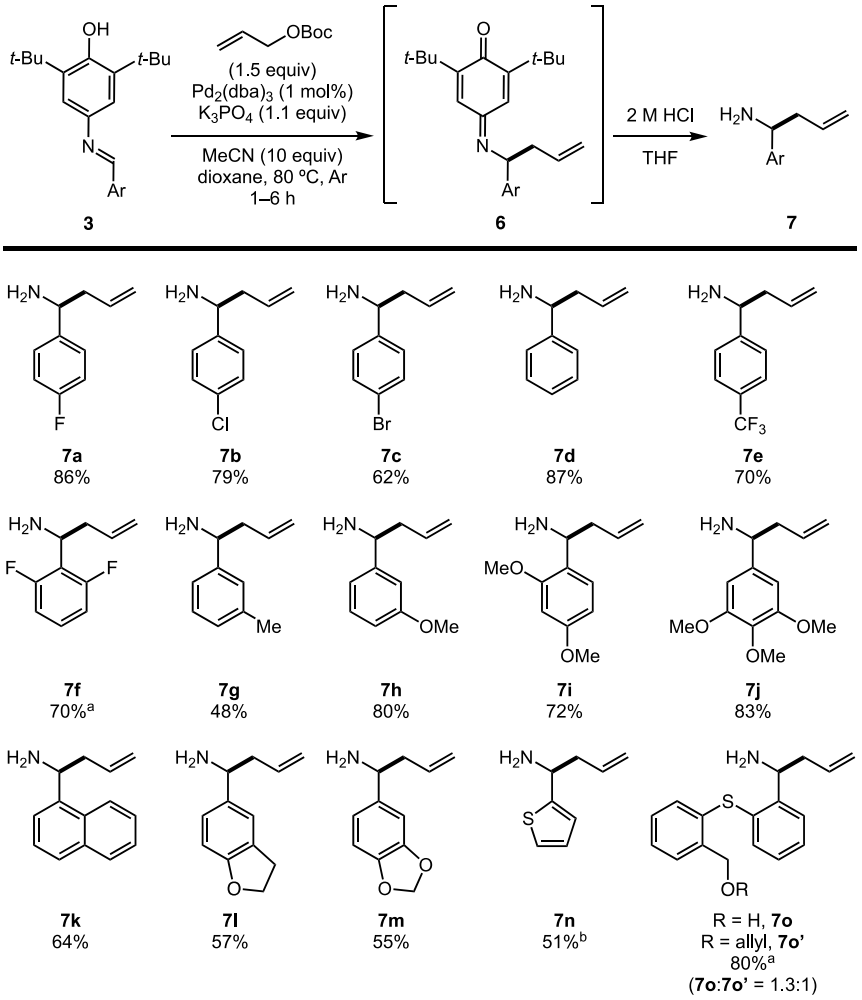
Table 2. Scope of *N*-(Aryloxy)imines 3 in the Dearomative, Pd-Catalyzed Allylation with Allyl *tert*-Butyl Carbonate



[a]Xantphos (2.5 mol %) was used instead of MeCN. [b]Reaction run at 90 °C.

isomeric products. Interestingly, decreasing the catalyst loading from 5 to 2 mol % led to virtually the same yield of **6a** (69%, entry 5) but an increased yield of isomeric allylic products. Evaluation of other solvents typically led to lower yields. For instance, ethereal solvents such as tetrahydrofuran (THF) and dioxane (entries 6 and 7) led to low yields of the desired product **6a**; however, dioxane provided the highest regioisomeric ratio (>10:1). The use of a 1:1 mixture of dioxane/MeCN led to a significant increase in yield with concomitant loss of regioselectivity (entry 8). Fortunately, further increasing the temperature to 80 °C led to an improvement of the regioselectivity (entry 9) albeit with a slightly lower yield of **6a** (73%). Adjusting the amount of MeCN to only 10 equiv provided **6a** in comparable yield at 50 °C (76%, entry 10) and increasing the temperature under these conditions led to an improved yield (89%, entry 11). Further reducing the amount of catalyst to 1 mol % had a negligible effect on the yield and regioselectivity (89%, 9:1 regioselectivity, entry 12). Finally, we demonstrated that the reaction does not proceed by direct attack of the *N*-(aryloxy)imine nucleophile on the allylic carbonate, as no conversion of **3a** was observed in the absence of Pd (entry 13).

Having established optimal conditions for the key bond-forming event, we then developed a hydrolytic workup protocol that would allow direct access to the desired amine products **7**. Accordingly, following the Pd-catalyzed allylation under the optimized conditions, the crude reaction mixture was treated with 2 M $HCl_{(aq)}$ in THF. After extraction and column chromatography, the desired amine product **7a** was isolated in 86% yield (Table 2). With this protocol in hand, we next evaluated the efficiency of this process using other *N*-(aryloxy)imines in reactions with allyl *tert*-butyl carbonate. Chloro and bromo substitutions were tolerated (**7b** and **7c**, 79 and 62%, respectively), although the latter was obtained in modest yield, presumably because of competitive oxidative addition to the C−Br bond. Electron-neutral (**7d**, 87%) and electron-deficient substrates (**7e**, 70%) were also competent reaction partners. 2,6-Difluoro substitution initially failed to provide any of the expected product, presumably because of slow electrophile trapping resulting from the attenuated nucleophilicity of this electronically deactivated substrate. However, we found that replacing acetonitrile with Xantphos allowed the desired allylation to take place efficiently (**7f**, 70%).[17,18] 3-Methyl substitution was tolerated, but led to modest yield of the desired product (**7g**, 48%). Electron-rich substrates also underwent efficient allylation under the standard reaction conditions (**7h**, **7i**, and **7j**; 80, 72, and 83%, respectively). 1-Naphthyl substituted (**7k**, 64%) and several heterocyclic homoallylic amines (**7l**, **7m**, **7n**; 57, 55, and 51%, respectively) could also be accessed using this

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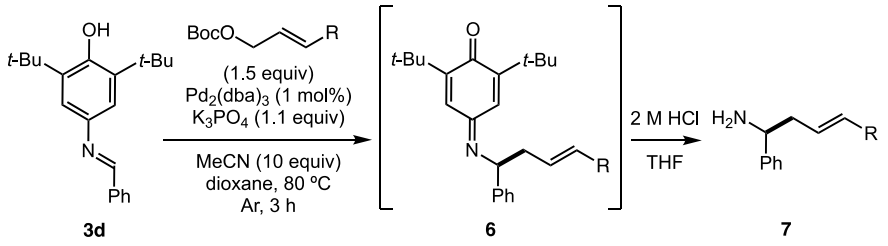
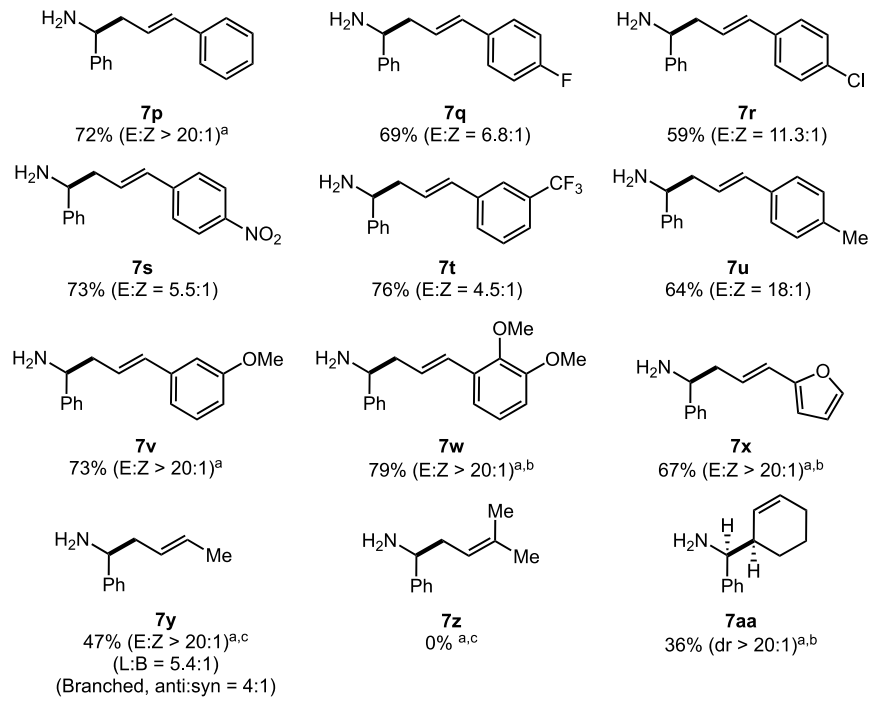
Table 3. Scope of Allylic Carbonates in the Dearomative, Pd-Catalyzed Allylation of *N*-(Aryloxy)imine 3d





[a]Reaction run at 90 °C. [b]Xantphos (2.5 mol %) was used instead of MeCN. [c]2 equiv of prenyl carbonate was used.

protocol. Finally, an *ortho* arylsulfide substituent bearing a benzylic alcohol was also tolerated; however, the use of Xantphos as a ligand was required to achieve productive reaction (80% overall), and competitive O-allylation (**7o** and **7o′**, 45 and 35%, respectively) was observed.

We then explored the scope of allyl carbonates that could function as electrophiles in the dearomative, Pd-catalyzed allylation of *N*-(aryloxy)imine **3d** (Table 3). Cinnamyl *tert*-butyl carbonate successfully participated in the reaction to give **7p** in 72% yield as a >20:1 mixture of *E*/*Z* isomers. Halogenated cinnamyl electrophiles were tolerated affording **7q** (69%, *E*/*Z* = 6.8:1) and **7r** (59%, *E*/*Z* = 11.3:1). More electron-deficient cinnamyl carbonates bearing nitro and trifluoromethyl substituents at the aromatic ring provided products **7s** and **7t** in good yields (73 and 76%, respectively) albeit with modest *E*/*Z* selectivities (5.5:1 and 4.5:1, respectively). Electron-donating groups on the aryl ring of the cinnamyl electrophile such as methyl (**7u**, 64%, *E*/*Z* = 18:1) and methoxy (**7v**, 73%, *E*/*Z* = 20:1) were tolerated and afforded the products with high *E*/*Z* selectivities. However, the 2,3-dimethoxy cinnamyl carbonate required both the use of higher temperature and Xantphos as a ligand to obtain a good yield of product **7w** (79%, *E*/*Z* = 20:1). This was necessary to overcome the higher energy barriers associated with oxidative addition to a more electron-rich allylic carbonate and nucleophilic attack of the azaallyl anion on a less-electrophilic allylpalladium species. Furyl-substituted electrophile required similar conditions to afford product **7x** (67%, *E*/*Z* = 20:1). Methyl-substituted allylic carbonate did not provide the desired allylation product under the standard reaction conditions; however, the use of Xantphos allowed access to **7y** in modest yield (47%) as a 5.4:1 mixture of linear and branched isomers, the latter of which was formed with modest diastereoselectivity (anti/syn = 4:1). Not surprisingly, reaction of a prenyl carbonate did not provide any of the desired product **7z** under the present conditions, presumably because of the relatively high barrier for this substrate to engage in oxidative addition. Notably, a cyclic allylic electrophile was tolerated and provided homoallylic amine **7aa** in 36% yield with excellent diastereoselectivity (>20:1).

Mechanistically, the desired C−C bond formation could take place by direct regioselective addition of the deprotonated *N*-(aryloxy)imine, a "soft" nucleophile ($pK_a \sim 10$),[19] to the Pd-π-allyl species (outer-sphere mechanism).[20] However, the propensity of this highly delocalized anion to react with a high level of regioselectivity to deliver the desired product **6** was not easily explained. In fact, early optimization studies revealed that undesired regioisomeric products ***C3-iso-6***, ***C5-iso-6***, and ***O-iso-6*** were formed in high concentrations at lower temperatures, whereas the desired product **6** was the major

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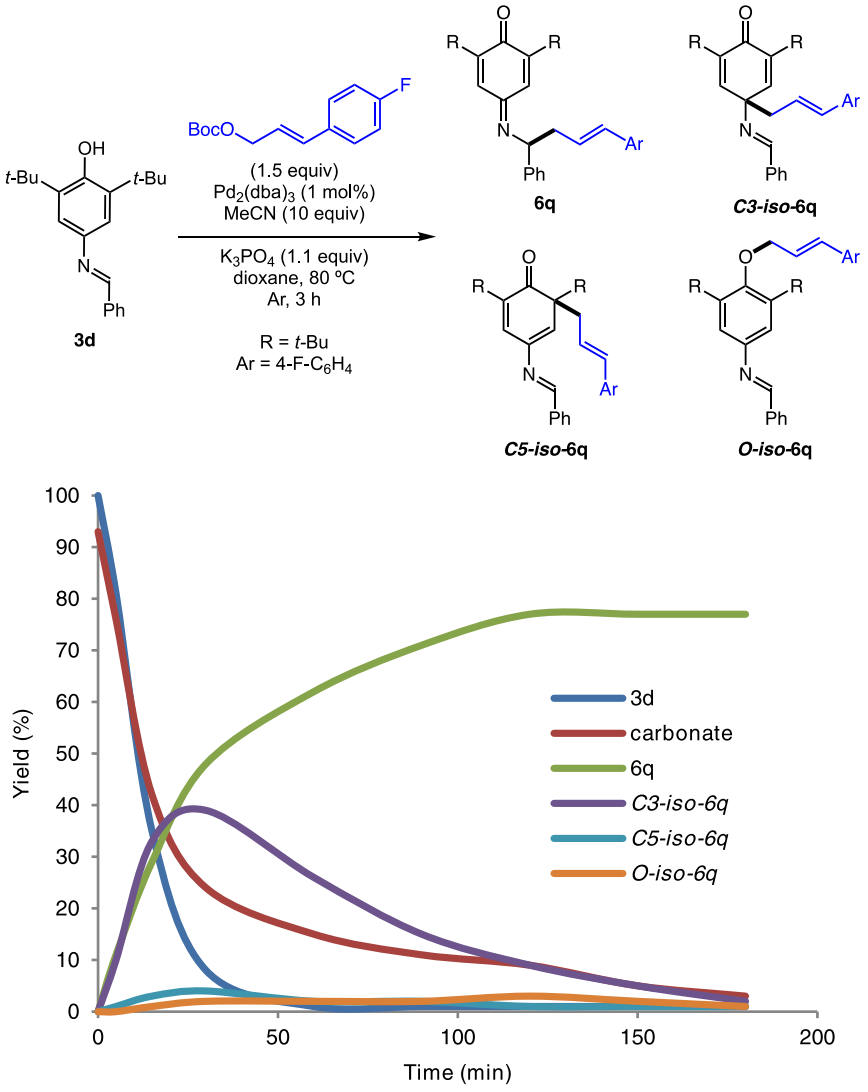
Scheme 4. Reaction Progress Followed by NMR Shows High Concentrations of Isomeric Products at Early Reaction Times



regioisomer at higher temperatures. To study this further, the reaction between **3d** and 4-fluorocinnamyl *tert*-butyl carbonate under standard conditions (80 °C, dioxane) was monitored as a function of time. This experiment revealed that isomeric allylic products (***C3-iso-6q***, ***C5-iso-6q***, and ***O-iso-6q***) were present in substantial quantities at early reaction times (0−30 min, Scheme 4). The isomeric allylated product ***C3-iso-6q***, in particular, reached 39% NMR yield after 30 min under these conditions. Interestingly, the concentration of this isomeric product gradually decreased over the next 2.5 h as the yield of the desired product (**6q**) increased up to a maximum of 77% NMR yield. At this point, the overall yield of isomeric allylated products (i.e., the sum of ***C3-iso-6q***, ***C5-iso-6q***, and ***O-iso-6q***) was only 4%. Notably absent in this reaction were any branched allylated products.

These observations led us to consider an alternative mechanism involving an unselective C−C bond-forming event between the *N*-(aryloxy)imine and the Pd-π-allyl species to form several allylated products, followed by convergent isomerization of some of these intermediates to the desired product **6**. Such convergent isomerizations to **6** could, in principle, take place via one of three mechanisms: (1) a Pd-catalyzed rearrangement via an associative or dissociative pathway,[21,22] (2) a concerted, thermal [3,3]-sigmatropic rearrangement,[18d,23] or (3) a stepwise process involving homolytic C−C bond cleavage and radical recombination.[24] Given that all isomeric allylated products ***C3-iso-6q***, ***C5-iso-6q***, and ***O-iso-6q*** were linear isomers, the possibility of concerted [3,3]-sigmatropic rearrangements was limited to only one regioisomer (***C5-iso-6q***), which would need to undergo two sequential [3,3]-sigmatropic rearrangements to give the observed linear allylation product **6q**. On the other hand, isomers ***C3-iso-6q*** and ***O-iso-6q*** would have to undergo rearrangement via a dissociative pathway to deliver the observed linear allylation product **6q**.

To shed light on the mechanism of this rearrangement, we isolated several isomeric products (***C3-iso-6q***, ***C3-iso-6y***, and ***C3-iso-6d***) derived from the reaction of *N*-(aryloxy)imine **3d** with 4-fluorocinnamyl, methallyl, and allyl carbonates. These isomeric products were the major competitive isomers observed in these reactions. We independently subjected them to the standard reaction conditions, in the presence or absence of Pd, to assess their ability to undergo isomerization to the corresponding iminoquinones (**6**, Table 4). These intermediates were differentiated by the substitution at the terminal olefin position, and were chosen to evaluate their

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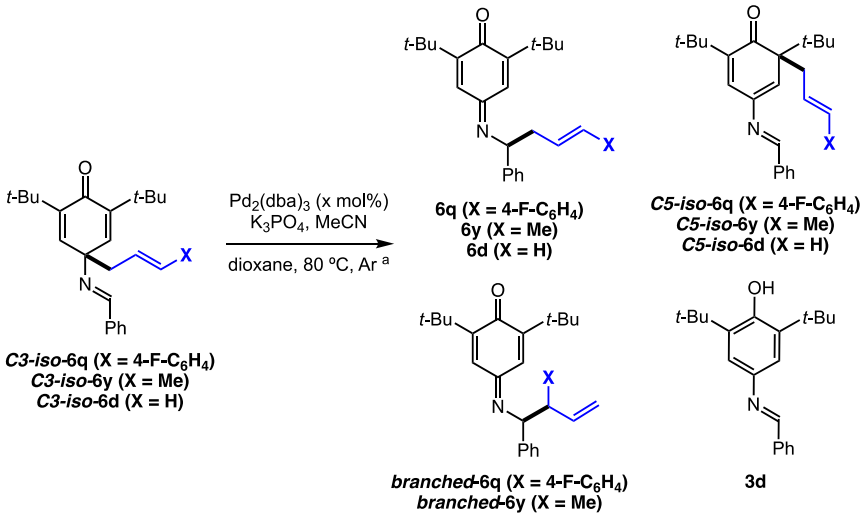
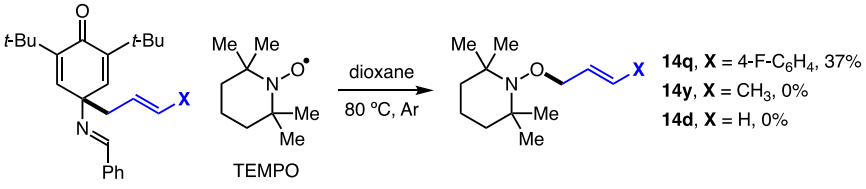
Table 4. Isomerization of *C3-iso*-6 in the Presence and Absence of Palladium



entry	X	$Pd_2(dba)_3$ (mol %)	conv. (%)	**6** (%)	**branched-6** (%)	***C5-iso*-6** (%)	**3d** (%)
1	4-F-C_6H_4	1	79	46	0	1	18
2	4-F-C_6H_4		78	39	0	3	22
3[b]	CH_3	1	100	17	4	0	76
4[b]	CH_3		75	0	50	0	0
5[c]	H	1	63	25		20	0
6[c]	H		63	19		18	0

[a]For detailed reaction conditions, see the Experimental Section. [b]Xantphos (2.5 mol %) was used instead of MeCN. [c]Trace quantities of the *O*-allyl isomer were observed.

Scheme 5. TEMPO-Trapping Experiments



ability to undergo isomerization in the absence of substitution (***C3-iso*-6d**), or in the presence of aryl (***C3-iso*-6q**) or methyl (***C3-iso*-6y**) substituents. The latter two substrates (***C3-iso*-6q** and ***C3-iso*-6y**) were expected to be particularly informative because they could distinguish between a stepwise (dissociative) or concerted (associative) mechanism for the observed rearrangement.

Thus, in the presence of Pd, isomeric product ***C3-iso*-6q** underwent rearrangement to give **6q** in 46% yield, together with trace amounts of the linear C5 product (***C5-iso*-6q**) and 18% yield of *N*-(aryloxy)imine **3d**, the latter formed as a consequence of deallylation (Table 4, entry 1). Importantly, in the absence of Pd, these isomerizations took place at virtually the same rate and led to the same distribution of products (entry 2), proving that Pd is not involved in the sigmatropic rearrangements that lead to the desired product. In addition, the exclusive formation of the linear product **6q** indicated that the isomerization involved a stepwise (dissociative) mechanism, which likely occurs via C−C bond homolysis and radical recombination. Indeed, heating ***C3-iso*-6q** in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) at 80 °C in dioxane led to the formation of the cinnamyl TEMPO adduct **14q** in 37% yield (Scheme 5), indicating that a radical mechanism for the observed rearrangement is operative. On the other hand, crotyl-derived compound ***C3-iso*-6y** underwent rearrangement in the presence of Pd and Xantphos to give a mixture of both linear and branched products (21% yield, 4.25:1.0 ratio), accompanied by a significant amount of deallylated product **3d** (76% yield). Surprisingly, in the absence of Pd, ***C3-iso*-6y** underwent exclusive [3,3]-sigmatropic rearrangement to give the branched product **branched-6y** in 50% yield without formation of deallylated product **3d**. These experiments suggest that Pd can mediate the isomerization of certain C3 isomers to the desired products albeit with significant deallylation taking place. However, crotyl-derived C3 isomers exclusively undergo concerted [3,3]-sigmatropic rearrangements in the absence of Pd. As supporting evidence, heating ***C3-iso*-6y** in the presence of TEMPO (80 °C, dioxane) led again to clean isomerization to the branched product (**branched-6y**, 65%) without formation of any crotylated TEMPO adduct as determined by both NMR and high-resolution mass spectrometry (HRMS) analyses (Scheme 5). This suggests that the mechanism by which ***C3-iso*-6q** and ***C3-iso*-6y** undergo thermal isomerization differs, presumably owing to the difference in stability of the corresponding allylic radicals that would have to form when

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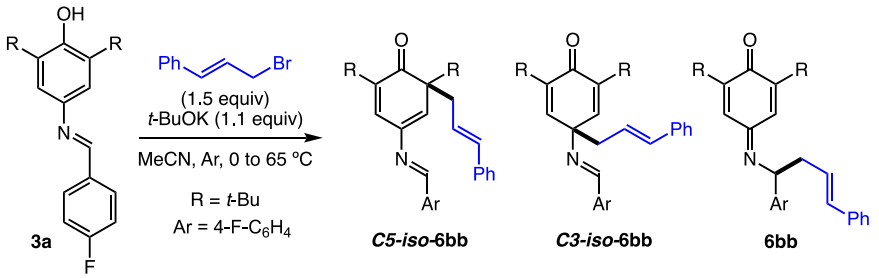
Table 5. Allylation of 3a with Cinnamyl Bromide and Subsequent [1,3]-Sigmatropic Rearrangement via a Dissociative Mechanism



entry	temperature	time	*C5-iso*-**6bb** (%)	*C3-iso*-**6bb** (%)	**6bb** (%)
1	0 °C	20 min	79	8	13
2	0 °C to rt	2 h	78	8	14
3	rt to 65 °C	2 h	2	4	92

the homolytic mechanism is operative. We also evaluated the isomerization of the unsubstituted allyl-derived compound ***C3-iso*-6d**. Here, we observed the formation of the desired product **6d** together with significant amounts of C5 allylated product ***C5-iso*-6d** in virtually the same yields with the same conversion in the presence or absence of Pd (entries 5 and 6). Therefore, the isomerization of unsubstituted ***C3-iso*-6d**-type intermediates does not require Pd. In addition, these rearrangements are likely concerted, as no deallylation product was observed. As supporting evidence, the trapping experiment with TEMPO led to rearrangement without formation of the TEMPO allyl adduct. These results suggest that initial Pd-mediated allylation provides a number of regioisomeric products with modest kinetic selectivity; however, the various regioisomers are capable of undergoing rearrangement to the desired, presumably thermodynamic, product through one of three mechanisms where the operative mechanism is dependent on both the substrate and the reaction conditions employed.

Further evidence demonstrating that the observed isomerization is not limited to the C3 isomer and that Pd is not required for this process was obtained as outlined in Table 5. When the anion generated from **3a** was treated with cinnamyl bromide at 0 °C, a mixture of allylated products was observed by ^{1}H NMR in which the C5 product (***C5-iso*-6bb**) was the major component (entry 1). Upon warming the reaction mixture to room temperature (rt), little change was observed (entry 2), but heating to 65 °C led to almost complete isomerization to the desired isomer **6bb** (entry 3, 92%). Presumably, this rearrangement occurs via a stepwise (dissociative) [1,3]-sigmatropic rearrangement (as shown in Table 4); however, we cannot rule out the possibility that this reaction might proceed via consecutive, concerted [3,3]-sigmatropic rearrangements. This result also indicates that it might be possible to develop a palladium-free variant of the chemistry reported herein.

Taken together, our experiments suggest that our allylation methodology proceeds by a mechanism involving the initial attack of *N*-(aryloxy)imine on the Pd-π-allyl electrophile to form several regioisomeric products. The kinetic regioselectivity of this step typically favors the desired product and ***C3-iso*-6**-type intermediates over ***C5-iso*-6**-type or ***O-iso*-6**-type intermediates. Following a relatively unselective kinetic allylation, rearrangement of the undesired regioisomers occurs to funnel material toward the desired regioisomer of the product, which is the presumed thermodynamic product of this process.

CONCLUSIONS

In conclusion, we have developed a stepwise protocol for the allylation of (pseudo)benzylic amines that proceeds by dearomative, Pd-catalyzed allylation of *N*-(aryloxy)imines to afford homoallylic amines in good yields. Our protocol is compatible with diverse *N*-(aryloxy)imines and allylic *tert*-butyl carbonates, thereby enabling access to a wide range of homoallylic amines. Our studies suggest that the kinetic products of C−C bond formation between the *N*-(aryloxy)-imines and the Pd-π-allyl electrophiles consist of a mixture of the desired product and other regioisomeric products. Mechanistic experiments demonstrate that these regioisomeric products undergo thermal rearrangement by one of two mechanisms: (1) homolytic C−C bond cleavage followed by recombination, or (2) concerted [3,3]-sigmatropic rearrangement; the operative mechanism appears to be substrate dependent. Reactions involving Xantphos[25] as a ligand allow Pd to catalyze the isomerization of C3 allyl intermediates, albeit with competitive, unproductive deallylation. This work has established for the first time that *N*-(aryloxy)imines can function as 2-azaallyl anion-like nucleophiles and are compatible with Pd(0)/Pd(II) catalysis. We expect to report related reactions of *N*-(aryloxy)imines with other electrophiles in due course.

EXPERIMENTAL SECTION

General Information. Reactions were run in oven-dried or flame-dried glassware under an argon atmosphere and stirred magnetically. Acetonitrile, THF, diethyl ether, and dichloromethane were purified by passing the solvent through activated alumina using a solvent purification system. Unless otherwise noted, purification of the products was carried out by flash chromatography using silica gel (230−400 mesh, Grade 60). Reactions were monitored by thin layer chromatography (TLC) (silica gel 60 F_{254}) and visualized using UV or $KMnO_4$, phosphomolybdic acid, and ceric ammonium molybdate stain solutions. ^{1}H NMR and ^{13}C NMR were recorded at rt in a Bruker 400, Bruker 500, or Bruker 600 instrument. Chemical shifts are reported in ppm and referenced with respect to residual protic solvents: chloroform at 7.26 ppm (^{1}H NMR); and the carbon resonances of the solvent: chloroform at 77.16 ppm (^{13}C NMR). The following abbreviations were used to refer to multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, and m = multiplet. Infrared spectra were recorded using a Shimadzu FTIR-

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8400S spectrometer. Mass spectra were obtained on a Micromass LCT Premier quadrupole and time-of-flight tandem mass analyzer.

Preparation of *N*-(Aryloxy)imines—General Procedure A. To a 100 mL round bottom flask were added a magnetic stir bar, 2,6-di-*tert*-butyl-1,4-benzoquinone (1 equiv), and EtOH (reaction concentration = 0.8−1.0 M). The flask was sealed with a septum, flushed with Ar, and the corresponding benzylic amine (1 equiv) was added using a syringe. The reaction was heated in an oil bath to 80 °C and the reaction followed by ^{1}H NMR until the ratio of iminophenol/*N*-benzylimine was maximized. The reaction was cooled to rt and left undisturbed until the product precipitated. The solid was filtered and recrystallized from warm hexanes or EtOAc/hexanes. The filtrate was concentrated and recrystallization from hexanes or EtOAc/hexanes was attempted. If no precipitation took place, the crude reaction mixture was partially concentrated and left to crystallize at rt. In a few cases, the desired product did not precipitate; in these cases, the products were partially purified by column chromatography (typically, 5% EtOAc in hexanes, buffered with 1% Et_3N) followed by recrystallization from hexanes or EtOAc/hexanes.

Preparation of *N*-(Aryloxy)imines—General Procedure B. To a 100 mL round bottom flask were added a magnetic stir bar and 4-amino-2,6-di-*tert*-butylphenol hydrochloride[26] (5 mmol, 1 equiv) (obtained by reduction of 2,6-di-*tert*-butyl-4-(hydroxyimino)-cyclohexa-2,5-dien-1-one[27]). Benzene (25 mL) was added to the flask and the flask was flushed with Ar. The corresponding benzaldehyde derivative (5 mmol, 1 equiv) and anhydrous K_2CO_3 (15 mmol, 3 equiv) were quickly added. The flask was equipped with a Dean−Stark trap and flushed with Ar. The reaction was subjected to reflux and followed by ^{1}H NMR. The reaction was cooled to rt and filtered to remove solids. Iminophenol product was obtained as crystals after concentrating the filtrate, followed by trituration with hexanes. The product was purified by recrystallization from hot hexanes.

Preparation of 2,6-Di-*tert*-butyl-4-((4-fluorobenzylidene)-amino)phenol (3a). Following General Procedure A, 4-fluorobenzylamine (3 g, 23.97 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (5.27 g, 23.97 mmol, 1 equiv), and EtOH (25 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 3.77 g (48%) of **3a** as light orange crystals. mp 135−137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.93−7.85 (m, 2H), 7.15 (t, J = 8.7 Hz, 2H), 7.11 (s, 2H), 5.19 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.6 (d, J = 250.8 Hz), 156.4, 152.8, 143.6, 136.9, 133.2 (d, J = 3.5 Hz), 130.5 (d, J = 9.0 Hz), 117.9, 116.0 (d, J = 21.9 Hz), 34.7, 30.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −109.1. FTIR: 3625, 2957, 1621, 1589, 1432, 823 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{21}H_{27}FNO]^+$, 328.2071; found, 328.2065.

Preparation of 2,6-Di-*tert*-butyl-4-((4-chlorobenzylidene)-amino)phenol (3b). Following General Procedure A, 4-chlorobenzylamine (1.93 g, 13.62 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3 g, 13.62 mmol, 1 equiv), and EtOH (25 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 1.84 g (39%) of **3b** as light yellow crystals. mp 135−137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.85−7.80 (m, 2H), 7.45−7.41 (m, 2H), 7.12 (s, 2H), 5.21 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.1, 152.8, 143.3, 136.7, 135.2, 129.7, 129.0, 117.9, 34.6, 30.3. FTIR: 3630, 2955, 1623, 1589, 1432, 823 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{21}H_{27}ClNO]^+$, 344.1781; found, 344.1770.

Preparation of 2,6-Di-*tert*-butyl-4-((4-bromobenzylidene)-amino)phenol (3c). Following General Procedure A, 4-bromobenzylamine (2.53 g, 13.62 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3 g, 13.62 mmol, 1 equiv), and EtOH (25 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 1.61 g (30%) of **3c** as light yellow crystals. mp 153−154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.12 (s, 2H), 5.22 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.2, 152.9, 143.2, 136.7, 135.6, 132.0, 130.0, 125.2, 117.9, 34.6, 30.3. FTIR: 3632, 2955, 1622, 1585, 1433, 819 cm^{-1}. HRMS m/z: calcd for $[C_{21}H_{27}BrNO]^+$, 388.1276; found, 388.1286.

Preparation of 2,6-Di-*tert*-butyl-4-(benzylideneamino)-phenol (3d). Following General Procedure A, benzylamine (2.48 mL, 9.078 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (5 g, 9.078 mmol, 1 equiv), and EtOH (23 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 2.24 g (60%) of **3d** as light yellow crystals. mp 149−151 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.89 (dd, J = 6.8, 2.9 Hz, 2H), 7.46 (dd, J = 4.9, 1.9 Hz, 3H), 7.13 (s, 2H), 5.19 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 158.0, 152.7, 143.8, 136.81, 136.79, 131.0, 128.9, 128.7, 118.0, 34.7, 30.4. FTIR: 3146, 2954, 1636, 1437 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{21}H_{28}NO]^+$, 310.2171; found, 310.2175.

Preparation of 2,6-Di-*tert*-butyl-4-((4-trifluoromethylbenzylidene)amino)phenol (3e). Following General Procedure B, 4-(trifluoromethyl)benzaldehyde (683 μL, 5 mmol, 1 equiv), 4-amino-2,6-di-*tert*-butylphenol hydrochloride (1.29 g, 5 mmol, 1 equiv), benzene (25 mL), and K_2CO_3 (15 mmol, 3 equiv, 2.07 g) afforded, after recrystallization from hexanes, 793.2 mg (42%) of **3e** as light orange crystals. mp 114−117 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.01 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.16 (s, 2H), 5.26 (s, 1H), 1.49 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.6, 153.2, 142.9, 139.8, 136.8, 132.2 (q, J = 32.3, 31.2 Hz), 128.6, 125.7 (q, J = 3.5 Hz), 124.0 (q, J = 272.2 Hz), 118.0, 34.6, 30.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.70. FTIR: 3636, 2957, 1621, 1579, 1434, 1323, 836 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{22}H_{27}F_3NO]^+$, 378.2045; found, 378.2048.

Preparation of 2,6-Di-*tert*-butyl-4-((2,6-difluorobenzylidene)amino)phenol (3f). Following General Procedure A, 2,6-difluorobenzylamine (2 g, 13.98 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3.08 g, 13.98 mmol, 1 equiv), and EtOH (18 mL) at 80 °C for 2 h afforded, after recrystallization from hexanes, 2.13 g (44%) of **3f** as orange crystals. mp 164−166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.36 (tt, J = 8.4, 6.1 Hz, 1H), 7.13 (s, 2H), 7.02−6.94 (m, 2H), 5.24 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 162.1 (dd, J = 6.4, 257.6 Hz), 153.3, 148.6, 144.2, 136.8, 131.8 (t, J = 10.9 Hz), 118.1, 114.6 (t, J = 12.7 Hz), 112.2 (dd, J = 4.6, 20.3 Hz), 34.7, 30.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −112.9. FTIR: 3610, 2954, 1622, 1462, 1017. HRMS (ESI) m/z: calcd for $[C_{21}H_{26}F_2NO]^+$, 346.1982; found, 346.1995.

Preparation of 2,6-Di-*tert*-butyl-4-((3-methylbenzylidene)-amino)phenol (3g). Following General Procedure A, *m*-tolylmethanamine (1.7 mL, 13.62 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3 g, 13.62 mmol, 1 equiv), and EtOH (18 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 1.9 g (43%) of **3g** as bright red crystals. mp 97−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.75 (d, J = 1.9 Hz, 1H), 7.68−7.62 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.30−7.26 (m, 1H), 7.12 (s, 2H), 5.18 (s, 1H), 2.44−2.40 (m, 3H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 158.1, 152.5, 143.8, 138.5, 136.65, 136.60, 131.7, 128.7, 128.6, 126.1, 117.8, 34.6, 30.3, 21.3. FTIR: 3634, 2955, 2912, 1624, 1583, 1433, 888 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{22}H_{30}NO]^+$, 324.2327; found, 324.2337.

Preparation of 2,6-Di-*tert*-butyl-4-((3-methoxybenzylidene)amino)phenol (3h). Following General Procedure A, 3-methoxybenzylamine (2 g, 14.58 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3.2 g, 14.58 mmol, 1 equiv), and EtOH (18 mL) at 80 °C for 7 h afforded, after recrystallization from hexanes, 2.01 g (41%) of **3h** as an orange solid. mp 117−119 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.52 (dd, J = 2.7, 1.4 Hz, 1H), 7.43−7.33 (m, 2H), 7.13 (s, 2H), 7.05−6.99 (m, 1H), 5.19 (s, 1H), 3.89 (s, 3H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.1, 157.8, 152.8, 143.7, 138.3, 136.8, 129.8, 122.1, 117.98, 117.96, 111.7, 55.6, 34.7, 30.4. FTIR: 3628, 2953, 1597, 1431 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{22}H_{30}NO_2]^+$, 340.2277; found, 340.2288.

Preparation of 2,6-Di-*tert*-butyl-4-((2,4-dimethoxybenzylidene)amino)phenol (3i). Following General Procedure A, 2,4-dimethoxybenzylamine (2 g, 11.96 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (2.6 g, 11.96 mmol, 1 equiv), and EtOH (13 mL) at 80 °C for 12 h afforded, after recrystallization from

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hexanes, 2.24 g (51%) of **3i** as light orange crystals. mp 124−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (s, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.07 (s, 2H), 6.57 (dd, J = 8.6, 2.3 Hz, 1H), 6.47 (d, J = 2.3 Hz, 1H), 5.11 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 1.47 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.4, 160.8, 154.0, 152.1, 145.0, 136.7, 128.8, 118.9, 118.0, 105.7, 98.2, 55.7, 55.6, 34.7, 30.5. FTIR: 3627, 2955, 1605, 1431, 1033 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{23}H_{32}NO_3]^+$, 370.2382; found, 370.2383.

Preparation of 2,6-Di-*tert*-butyl-4-((3,4,5-trimethoxybenzylidene)amino)phenol (3j). Following General Procedure A, 3,4,5-trimethoxybenzylamine (1.8 g, 9.08 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (2 g, 9.08 mmol, 1 equiv), and EtOH (20 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 1.14 g (31%) of **3j** as light brown crystals. mp 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.15 (s, 2H), 7.11 (s, 2H), 5.19 (s, 1H), 3.95 (s, 6H), 3.91 (s, 3H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.1, 153.5, 152.5, 143.5, 140.5, 136.7, 132.2, 117.8, 105.5, 61.0, 56.3, 34.5, 30.3. FTIR: 3630, 2998, 2954, 1620, 1578, 1432, 1329, 805 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{24}H_{34}NO_4]^+$, 400.2488; found, 400.2501.

Preparation of 2,6-Di-*tert*-butyl-4-((naphthalen-1-ylmethylene)amino)phenol (3k). Following General Procedure A, naphthalen-1-ylmethanamine (2 mL, 13.62 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3 g, 13.62 mmol, 1 equiv), and EtOH (30 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 1.76 g (36%) of **3k** as shiny, yellow, flaky crystals. mp 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (s, 1H), 8.98 (dq, J = 8.6, 1.0 Hz, 1H), 8.09 (dd, J = 7.1, 1.3 Hz, 1H), 7.94 (ddt, J = 14.0, 8.2, 0.9 Hz, 2H), 7.62 (ddd, J = 8.5, 6.8, 1.5 Hz, 1H), 7.60−7.53 (m, 2H), 7.20 (s, 2H), 5.22 (s, 1H), 1.51 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.5, 152.6, 144.5, 136.8, 133.9, 132.0, 131.5, 131.3, 129.0, 128.8, 127.3, 126.2, 125.4, 124.2, 117.9, 77.4, 77.0, 76.7, 34.6, 30.3. FTIR: 3627, 3055, 2955, 1626, 1587, 1431 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{25}H_{30}NO]^+$, 360.2327; found, 360.2336.

Preparation of 2,6-Di-*tert*-butyl-4-(((2,3-dihydrobenzofuran-5-yl)methylene)amino)phenol (3l). Following General Procedure A, 2,3-dehydro-5-benzofuranmethanamine (1.2 g, 8.04 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (1.77 g, 8.04 mmol, 1 equiv), and EtOH (10 mL) at 80 °C for 7 h afforded, after column chromatography (gradient 5−40% EtOAc in hexanes) and recrystallization from dichloromethane/hexanes, 623 mg (22%) of **3l** as a white solid. mp 136−137 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.85 (s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.08 (s, 2H), 6.84 (d, J = 8.2 Hz, 1H), 5.15 (s, 1H), 4.65 (t, J = 8.7 Hz, 2H), 3.26 (t, J = 8.7 Hz, 2H), 1.47 (s, 18H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 162.8, 157.8, 152.3, 144.2, 136.7, 130.7, 130.0, 128.2, 124.5, 117.8, 109.5, 72.1, 30.4, 29.5, 29.3. FTIR: 3622, 2954, 1608, 1429 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{23}H_{30}NO_2]^+$, 352.2277; found, 352.2277.

Preparation of 4-((Benzo[*d*][1,3]dioxo-5-ylmethylene)-amino)-2,6-di-*tert*-butylphenol (3m). Following General Procedure A, 3,4-(methylenedioxy)benzylamine (2 g, 13.23 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (2.91 g, 13.23 mmol, 1 equiv), and EtOH (14 mL) at 80 °C for 12 h afforded, after recrystallization from hexanes, 1.89 g (40%) of **3m** as light orange crystals. mp 170−171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.52 (d, J = 1.7 Hz, 1H), 7.26 (m, 1H), 7.09 (s, 2H), 6.88 (d, J = 7.9 Hz, 1H), 6.03 (s, 2H), 5.16 (s, 2H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.1, 152.5, 150.21, 148.5, 143.8, 136.8, 131.8, 125.3, 117.9, 108.3, 106.9, 101.7, 34.7, 30.42. FTIR: 3628, 2954, 1624, 1446, 1039 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{22}H_{28}NO_3]^+$, 354.2069; found, 354.2084.

Preparation of 2,6-Di-*tert*-butyl-4-((2-thiophen-2-ylmethylene)amino)phenol (3n). Following General Procedure A, thiophen-2-ylmethanamine (1.4 mL, 13.62 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (3 g, 13.62 mmol, 1 equiv), and EtOH (30 mL) at 80 °C for 16 h afforded, after recrystallization from hexanes, 2.34 g (54%) of **3n** as yellow crystals. mp 161−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 0.9 Hz, 1H), 7.45 (ddd, J = 5.2, 4.1, 1.1 Hz, 2H), 7.14−7.09 (m, 3H), 5.18 (s, 1H), 1.47 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.6, 150.5, 143.4, 143.1, 136.6, 131.2, 129.4, 127.7, 117.9, 34.6, 30.3. FTIR: 3626, 3195, 2951, 1606, 1579, 1428 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{19}H_{26}NOS]^+$, 316.1735; found, 316.1739.

Preparation of 2,6-Di-*tert*-butyl-4-((2-((2-(hydroxymethyl)-phenyl)thio)benzylidene)amino)phenol (3o). Following General Procedure A, (2-((2-(aminomethyl)phenyl)thio)phenyl)methanol (1.5 g, 6.12 mmol, 1 equiv), 2,6-di-*tert*-butyl-1,4-benzoquinone (1.35 g, 6.12 mmol, 1 equiv), and EtOH (7 mL) at 80 °C for 12 h afforded, after recrystallization from EtOAc/hexanes, 874 mg (32%) of **3o** as an orange solid. mp 116−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.95 (s, 1H), 8.15 (dd, J = 7.6, 1.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.39−7.29 (m, 3H), 7.25−7.20 (m, 2H), 7.15 (dd, J = 7.8, 1.5 Hz, 1H), 7.07 (s, 2H), 5.20 (s, 1H), 4.82 (s, 2H), 1.45 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 155.7, 153.0, 143.6, 141.4, 136.8, 136.5, 136.4, 133.5, 132.7, 132.1, 131.3, 128.9, 128.8, 128.2, 127.8, 118.2, 63.7, 34.6, 30.4. FTIR: 3629, 3059, 2954, 1615, 1431, 1031 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{28}H_{34}NO_2S]^+$, 448.2310; found, 448.2331.

Preparation of Allylic Carbonates and Precursors. *Preparation of Methyl Cinnamates—General Procedure C.* To a 100 mL round bottom flask were added a magnetic stir bar, the corresponding cinnamic acid (11 mmol), methanol (30 mL), and sulfuric acid (0.5 mL). A reflux condenser was attached and the reaction was heated to reflux overnight (12−16 h). The reaction was cooled to rt, diluted with ethyl acetate (100 mL), and washed with water (2 × 10 mL), $NaHCO_{3(sat)}$, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The crude product was used in the next step without further purification.

Preparation of Cinnamyl Alcohols—General Procedure D. To a dry 250 mL round bottom flask were added a magnetic stir bar, the corresponding methyl cinnamate (11 mmol, 1 equiv), and dichloromethane (90 mL, 0.12 M). The flask was flushed with Ar and cooled using an ice bath. diisobutylaluminum hydride (DIBAL) (3.9 mL, 22 mmol, 2 equiv) was added dropwise using a syringe. The ice bath was removed, and the reaction was monitored by TLC. After ∼2 h, the reaction was cooled to 0 °C and quenched with water (0.88 mL), followed by addition of 15% $NaOH_{(aq)}$ (0.88 mL). Water (2.2 mL) was added and the mixture was warmed to rt with stirring. After 15 min, ∼2 scoops of $MgSO_4$ were added and the mixture was stirred at rt for 30 min. The mixture was filtered through Celite, concentrated, and the product was purified by column chromatography.

Preparation of Allylic and Cinnamyl Carbonates—General Procedure E[3]. Following a reported procedure,[28] to a solution of the corresponding cinnamyl alcohol (1 equiv) in dichloromethane (reaction concentration ∼ 2.2 M) were added Boc anhydride (1.4 equiv) and Bu_4NHSO_4 (0.03 equiv). The solution was cooled to 0 °C and 30% $NaOH_{(aq)}$ (0.25 mL/mmol alcohol) was added dropwise with vigorous stirring. The reaction was followed by TLC. After ∼2 h, the reaction was diluted with dichloromethane (50 mL) and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. Column chromatography (5−10% EtOAc in hexanes) afforded the cinnamyl carbonates.

Preparation of (*E*)-*tert*-Butyl Cinnamyl Carbonate. Following General Procedure E, (*E*)-3-(phenyl)prop-2-en-1-ol (3.4 g, 25.34 mmol, 1 equiv), dichloromethane (15 mL), Boc anhydride (6.34 g, 29.1 mmol, 1.4 equiv), Bu_4NHSO_4 (228 mg, 0.67 mmol, 0.03 equiv), and 30% NaOH (6 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 4.78 g (80%) of (*E*)-*tert*-butyl cinnamyl carbonate as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.36 (m, 3H), 7.32 (ddd, J = 8.0, 6.9, 1.0 Hz, 3H), 7.28−7.23 (m, 2H), 6.67 (d, J = 15.9 Hz, 1H), 6.30 (dt, J = 15.9, 6.5 Hz, 1H), 4.72 (dd, J = 6.5, 1.3 Hz, 3H), 1.51 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.5, 136.3, 134.6, 128.7, 128.2, 126.8, 123.0, 82.4, 67.6, 27.9. Spectral data are in accordance with published values.[28]

Preparation of (*E*)-*tert*-Butyl-(3-(4-methylphenyl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(4-methylphenyl)-prop-2-en-1-ol (1.44 g, 9.72 mmol, 1 equiv), dichloromethane (5 mL), Boc anhydride (2.97 g, 13.6 mmol, 1.4 equiv), Bu_4NHSO_4 (99 mg, 0.291 mmol, 0.03 equiv), and 30% NaOH (2.4 mL) at 0 °C for

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2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 2.05 g (85%) of (*E*)-*tert*-butyl-(3-(4-methylphenyl)allyl) carbonate as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.66 (d, J = 15.8 Hz, 1H), 6.27 (dt, J = 15.8, 6.5 Hz, 1H), 4.73 (dd, J = 6.6, 1.3 Hz, 2H), 2.36 (s, 3H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.5, 138.2, 134.7, 133.6, 129.4, 126.7, 122.0, 82.3, 67.8, 27.9, 21.4. Spectral data are in accordance with published values.[29]

Preparation of (*E*)-*tert*-Butyl-(3-(4-fluorophenyl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(fluorophenyl)prop-2-en-1-ol (1.64 g, 10.78 mmol, 1 equiv), dichloromethane (5 mL), Boc anhydride (3.3 g, 15.1 mmol, 1.4 equiv), Bu_4NHSO_4 (110 mg, 0.327 mmol, 0.03 equiv), and 30% NaOH (2.7 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 1.99 g (73%) of (*E*)-*tert*-butyl-(3-(4-fluorophenyl)allyl) carbonate as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, J = 8.6, 5.5 Hz, 2H), 7.00 (t, J = 8.7 Hz, 2H), 6.63 (dd, J = 15.8, 1.6 Hz, 1H), 6.21 (dt, J = 15.9, 6.4 Hz, 1H), 4.70 (dd, J = 6.4, 1.4 Hz, 2H), 1.50 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.71, 153.47, 146.88, 133.38, 132.52, 132.50, 128.38, 128.32, 122.82, 122.80, 115.76, 115.58, 82.40, 77.41, 77.36, 77.16, 76.91, 67.46, 27.53. Spectral data are in accordance with published values.[29]

Preparation of (*E*)-*tert*-Butyl-(3-(4-chlorophenyl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(chlorophenyl)prop-2-en-1-ol (1.79 g, 10.62 mmol, 1 equiv), dichloromethane (3 mL), Boc anhydride (3.24 g, 14.86 mmol, 1.4 equiv), Bu_4NHSO_4 (108 mg, 0.319 mmol, 0.03 equiv), and 30% NaOH (2.6 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 2.21 g (77%) of (*E*)-*tert*-butyl-(3-(4-chlorophenyl)allyl) carbonate as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34−7.27 (m, 1H), 6.62 (dd, J = 15.9, 1.5 Hz, 0H), 6.27 (dt, J = 15.8, 6.4 Hz, 0H), 4.71 (dd, J = 6.4, 1.4 Hz, 0H), 1.50 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.5, 134.9, 133.9, 133.2, 128.9, 128.0, 123.8, 82.5, 67.4, 27.9. Spectral data are in accordance with published values.[30]

Preparation of (*E*)-*tert*-Butyl-(3-(3-methoxyphenyl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(methoxyphenyl)prop-2-en-1-ol (1.44 g, 8.77 mmol, 1 equiv), dichloromethane (3 mL), Boc anhydride (2.68 g, 12.28 mmol, 1.4 equiv), Bu_4NHSO_4 (89 mg, 0.263 mmol, 0.03 equiv), and 30% NaOH (4.4 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 2.15 g (93%) of (*E*)-*tert*-butyl-(3-(4-methoxyphenyl)allyl) carbonate as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (t, J = 7.9 Hz, 1H), 6.98 (dt, J = 7.8, 1.2 Hz, 1H), 6.95−6.88 (m, 1H), 6.82 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 6.64 (dt, J = 15.8, 1.4 Hz, 1H), 6.29 (dt, J = 15.8, 6.4 Hz, 1H), 4.72 (dd, J = 6.4, 1.4 Hz, 2H), 3.81 (s, 3H), 1.50 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 159.9, 137.8, 134.4, 129.7, 123.4, 119.5, 113.9, 112.01, 82.4, 67.5, 55.4, 27.9. Spectral data are in accordance with published values.[28]

Preparation of (*E*)-*tert*-Butyl-(3-(4-nitrophenyl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(4-nitrophenyl)prop-2-en-1-ol (1.79 g, 10 mmol, 1 equiv), dichloromethane (10 mL), Boc anhydride (3.2 mL, 14 mmol, 1.4 equiv), Bu_4NHSO_4 (101.9 mg, 0.3 mmol, 0.03 equiv), and 30% NaOH (2.5 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (5−15% EtOAc in hexanes), 1.29 g (46%) of (*E*)-*tert*-butyl-(3-(4-nitrophenyl)allyl) carbonate as a white solid. mp 78−79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22−8.15 (m, 2H), 7.55−7.48 (m, 2H), 6.73 (dt, J = 16.0, 1.6 Hz, 1H), 6.46 (dt, J = 16.0, 5.9 Hz, 1H), 4.76 (dd, J = 6.0, 1.5 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 153.2, 147.2, 142.6, 131.4, 128.0, 127.2, 124.1, 82.7, 66.6, 27.8. FTIR: 3106, 3078, 2984, 2936, 1738, 1516, 1458, 1374, 1343, 821 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{14}H_{18}NO_5]^+$, 280.1185; found, 280.1199.

Preparation of (*E*)-*tert*-Butyl-(3-(2,3-dimethoxyphenyl)allyl) Carbonate. Following General Procedure C, 2,3-dimethoxycinnamic acid (2.27 g, 11 mmol) in MeOH (30 mL) with sulfuric acid (0.5 mL) at reflux afforded, after workup, 2.33 g of methyl-2,3-dimethoxycinnamate (95%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 16.2 Hz, 1H), 7.15 (dd, J = 7.9, 1.4 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.94 (dd, J = 8.2, 1.4 Hz, 1H), 6.49 (d, J = 16.2 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.7, 153.3, 148.6, 139.7, 128.7, 124.3, 119.4, 119.3, 114.1, 61.5, 56.0, 51.8.

Following General Procedure D, (*E*)-methyl-2,3-dimethoxycinnamate (2.98 g, 10.3 mmol, 1 equiv) and DIBAL (3.74 mL, 20.9 mmol, 2 equiv) in dichloromethane (90 mL) afforded, after workup and column chromatography (10% EtOAc in hexanes), 1.85 g (91%) of (*E*)-2,3-dimethoxycinnamyl alcohol as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (dd, J = 7.9, 1.6 Hz, 1H), 7.01 (t, J = 8.0 Hz, 1H), 6.92 (dd, J = 16.0, 1.8 Hz, 1H), 6.82 (dd, J = 8.1, 1.5 Hz, 1H), 6.39 (ddd, J = 16.1, 6.7, 5.0 Hz, 1H), 4.53−4.21 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 1.58 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.1, 146.9, 130.95, 130.1, 130.1, 125.6, 125.5, 124.2, 118.4, 111.6, 64.2, 64.2, 61.0, 55.9. Spectral data are in accordance with published values.[31]

Following General Procedure E, (*E*)-2,3-dimethoxycinnamyl alcohol (1.83 g, 9.42 mmol, 1 equiv), dichloromethane (3 mL), Boc anhydride (2.88 g, 13.19 mmol, 1.4 equiv), Bu_4NHSO_4 (96 mg, 0.28 mmol, 0.03 equiv), and 30% NaOH (2.4 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 2.73 g (99%) of (*E*)-*tert*-butyl-(3-(2,3-dimethoxyphenyl)-allyl) carbonate as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10 (dd, J = 7.9, 1.5 Hz, 1H), 7.07−6.98 (m, 2H), 6.86 (dd, J = 8.1, 1.5 Hz, 1H), 6.34 (dt, J = 16.0, 6.5 Hz, 1H), 4.76 (dd, J = 6.4, 1.4 Hz, 2H), 3.88 (s, 3H), 3.83 (s, 2H), 1.53 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.5, 153.1, 147.1, 130.5, 129.0, 124.4, 124.2, 118.5, 112.0, 82.3, 68.0, 61.1, 55.9, 27.9. FTIR: 3061, 2983, 1742, 1585, 1483, 1240 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{16}H_{22}O_5Na]^+$, 317.1365; found, 317.1380.

Preparation of (*E*)-*tert*-Butyl-(3-(3-(trifluoromethyl)phenyl)-allyl) Carbonate. Following General Procedure C, (*E*)-3-(3-(trifluoromethyl)phenyl)acrylic acid (2.38 g, 11 mmol) in MeOH (30 mL) with sulfuric acid (0.5 mL) at reflux afforded, after workup, 2.58 g (100%) of methyl (*E*)-3-(3-(trifluoromethyl)phenyl)acrylate as an off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 2.1 Hz, 1H), 7.75−7.60 (m, 3H), 7.52 (t, J = 7.8 Hz, 1H), 6.51 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 167.0, 143.2, 135.3, 132.6 (q, J = 32.7 Hz), 131.2, 129.6, 126.8 (q, J = 3.7 Hz), 124.8 (q, J = 3.7 Hz), 123.9 (q, J = 273.1 Hz), 119.9, 52.1.

Following General Procedure D, (*E*)-3-(3-(trifluoromethyl)-phenyl)acrylate (2.58 g, 11 mmol, 1 equiv) and DIBAL (3.9 mL, 22 mmol, 2 equiv) in dichloromethane (90 mL) afforded, after workup and column chromatography (10% EtOAc in hexanes), 1.96 g (88%) of (*E*)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 2.0 Hz, 1H), 7.59−7.54 (m, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 6.66 (dt, J = 15.9, 1.7 Hz, 1H), 6.44 (dt, J = 15.9, 5.4 Hz, 1H), 4.36 (dd, J = 5.4, 1.7 Hz, 2H), 1.57 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.7, 131.2 (q, J = 32.0 Hz), 130.7, 129.7, 129.5, 129.2, 124.3 (q, J = 3.7 Hz), 123.2 (q, J = 273.0 Hz), 123.24 (q, J = 3.9 Hz), 63.5. Spectral data are in accordance with published values.[32]

Following General Procedure E, (*E*)-3-(3-(trifluoromethyl)-phenyl)prop-2-en-1-ol (1.96 g, 9.69 mmol, 1 equiv), dichloromethane (2.5 mL), Boc anhydride (2.96 g, 13.19 mmol, 1.4 equiv), Bu_4NHSO_4 (99 mg, 0.28 mmol, 0.03 equiv), and 30% NaOH (4.9 mL) at 0 °C for 4 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 2.61 g (89%) of (*E*)-*tert*-butyl-(3-(3-(trifluoromethyl)phenyl)allyl) carbonate as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 2.1 Hz, 1H), 7.59−7.53 (m, 1H), 7.53−7.48 (m, 1H), 7.44 (t, J = 7.7 Hz, 1H), 6.70 (dd, J = 16.0, 1.5 Hz, 1H), 6.36 (dt, J = 15.9, 6.2 Hz, 1H), 4.74 (dd, J = 6.2, 1.5 Hz, 2H), 1.51 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.4, 137.2, 132.7, 131.2 (q, J = 31.8 Hz), 129.9, 129.2, 125.2, 124.73 (q, J = 3.6 Hz), 124.2 (q, J = 273 Hz), 123.5 (q, J = 3.6 Hz), 82.6, 67.01, 27.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.8. FTIR: 3468, 2982, 1743, 1278, 1128 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{15}H_{18}F_3O_3]^+$, 303.1203; found, 303.1219.

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Preparation of (*E*)-*tert*-Butyl-(3-(furan-2-yl)allyl) Carbonate. Following General Procedure E, (*E*)-3-(furan-2-yl)prop-2-en-1-ol[33] (1.47 g, 11.84 mmol, 1 equiv), dichloromethane (3.1 mL), Boc anhydride (3.8 mL, 16.58 mmol, 1.4 equiv), Bu_4NHSO_4 (122.2 mg, 0.36 mmol, 0.03 equiv), and 30% NaOH (5.9 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (5−15% EtOAc in hexanes), 2.29 g (86%) of (*E*)-*tert*-butyl-(3-(furan-2-yl)allyl) carbonate as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 1.8 Hz, 1H), 6.47 (dt, J = 15.9, 1.4 Hz, 1H), 6.37 (dd, J = 3.4, 1.8 Hz, 1H), 6.28 (d, J = 3.3 Hz, 1H), 6.21 (dt, J = 15.8, 6.4 Hz, 1H), 4.68 (dd, J = 6.4, 1.4 Hz, 2H), 1.49 (s, 10H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 153.3, 151.9, 142.4, 122.3, 121.4, 111.3, 108.9, 82.2, 67.0, 27.8. Spectral data are in accordance with published values.[34]

Preparation of (*E*)-*tert*-Butyl(methallyl) Carbonate. Following General Procedure E, (*E*)-crotyl alcohol (0.77 mL, 9 mmol, 1 equiv), dichloromethane (2.3 mL), Boc anhydride (2.75 g, 12.6 mmol, 1.4 equiv), Bu_4NHSO_4 (92 mg, 0.27 mmol, 0.03 equiv), and 30% NaOH (4.5 mL) at 0 °C for 2.5 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 976 mg (63%) of (*E*)-*tert*-butyl-(methallyl) carbonate as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (dddd, J = 15.3, 7.6, 6.5, 5.4 Hz, 0H), 5.61 (dddd, J = 15.2, 8.3, 5.0, 1.6 Hz, 1H), 4.48 (dt, J = 6.6, 1.1 Hz, 1H), 1.80−1.65 (m, 1H), 1.48 (s, 5H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.6, 132.1, 125.0, 82.1, 27.9, 17.9. Spectral data are in accordance with published values.[29]

Preparation of *tert*-Butyl Cyclohex-2-en-1-yl Carbonate. Following General Procedure E, (*E*)-crotyl alcohol (1.0 mL, 10.2 mmol, 1 equiv), dichloromethane (6 mL), Boc anhydride (3.1 g, 14.3 mmol, 1.4 equiv), Bu_4NHSO_4 (100 mg, 0.305 mmol, 0.03 equiv), and 30% NaOH (2.5 mL) at 0 °C for 6 h afforded, after extraction and column chromatography (10% EtOAc in hexanes), 414 mg (21%) of *tert*-butyl cyclohex-2-en-1-yl carbonate as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.97 (dtd, J = 10.1, 3.8, 1.3 Hz, 1H), 5.79 (ddt, J = 10.1, 4.1, 2.2 Hz, 1H), 5.09 (dp, J = 5.2, 1.8 Hz, 1H), 2.15−1.93 (m, 2H), 1.93−1.73 (m, 3H), 1.70−1.60 (m, 1H), 1.51 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.5, 133.1, 125.5, 81.9, 70.9, 28.4, 28.0, 25.0, 18.9. Spectral data are in accordance with published values.[35]

Synthesis of Homoallylic Amines. *Palladium-Catalyzed Allylation of N-(Aryloxy)imines with Allyl tert-Butyl Carbonate—General Procedure F.* A flame-dried 10 mL Schlenk flask with a magnetic stir bar was charged with *N*-(aryloxy)imine (1 mmol, 1 equiv), $Pd_2(dba)_3$ (0.01 mmol, 0.01 equiv), and K_3PO_4 (1.1 mmol, 1.1 equiv). The flask was sealed with a septum and evacuated/backfilled with Ar (3 cycles). Then, dioxane (5 mL), MeCN (10 mmol, 10 equiv), and allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv) were added sequentially using a syringe. The reaction was heated in an oil bath to 80 °C with vigorous stirring. After 1 h, the reaction was cooled to rt, diluted with EtOAc (∼40 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL) and dried over Na_2SO_4. 1,3,5-Trimethoxybenzene (168.2 mg, 1 equiv) was added and the solution concentrated and analyzed by ^{1}H NMR to obtain an NMR yield of the allylation step.

The crude reaction mixture was then dissolved in THF (∼4 mL) and 2 M $HCl_{(aq)}$ (4 mL) was added. The reaction mixture was stirred at rt and hydrolysis of the iminoquinone product was monitored by TLC. After ∼2−3 h, the reaction was transferred to a separatory funnel using diethyl ether (10 mL) and water (∼5 mL) to rinse the flask. The aqueous phase was extracted with diethyl ether (5 mL). The combined organic extracts were washed with 1 M $HCl_{(aq)}$ (2 × 5 mL). The combined aqueous phases were basified with 3 M $NaOH_{(aq)}$ (pH > 10) and extracted with dichloromethane (4 × 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (1−10% MeOH in dichloromethane) afforded the homoallylic amine.

Palladium-Catalyzed Allylation of N-(Aryloxy)imines with Cinnamyl-Derived Carbonates—General Procedure G. A flame-dried 10 mL Schlenk flask with a magnetic stir bar was charged with *N*-(aryloxy)imine (1 mmol, 1 equiv), $Pd_2(dba)_3$ (0.01 mmol, 0.01 equiv), and K_3PO_4 (1.1 mmol, 1.1 equiv). If the allylic carbonate was a solid, it was added at this point. The flask was sealed with a septum and evacuated/backfilled with Ar (3 cycles). Then, dioxane (3.3 mL), MeCN (10 mmol, 10 equiv), and the cinnamyl *tert*-butyl carbonate (1.5 mmol, 1.5 equiv) were added sequentially using a syringe. The reaction was heated in an oil bath to 80 °C with vigorous stirring. After 3 h, the reaction was cooled to rt, diluted with EtOAc (∼40 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL) and dried over Na_2SO_4. 1,3,5-Trimethoxybenzene (168.2 mg, 1 equiv) was added and the solution was concentrated and analyzed by ^{1}H NMR to obtain an NMR yield of the allylation step.

The crude reaction mixture was then dissolved in THF (∼4 mL) and 2 M $HCl_{(aq)}$ (4 mL) was added. The reaction mixture was stirred at rt and hydrolysis of the iminoquinone product was monitored by TLC. After ∼2−3 h, the reaction was diluted with THF (15 mL) and transferred to a separatory funnel using diethyl ether (20 mL) and water (∼5 mL) to rinse the flask. The organic phase was washed with 1 M $HCl_{(aq)}$ (4 × 5 mL). The combined aqueous phases were basified with 3 M $NaOH_{(aq)}$ (pH > 10) and extracted with dichloromethane (4 × 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (1−10% MeOH in dichloromethane) afforded the cinnamyl-derived homoallylic amine.

Palladium-Catalyzed Allylation of N-(Aryloxy)imines with Less-Reactive Allylic Carbonates—General Procedure H. A flame-dried 10 mL Schlenk flask with a magnetic stir bar was charged with *N*-(aryloxy)imine (1 mmol, 1 equiv), $Pd_2(dba)_3$ (0.01 mmol, 0.01 equiv), Xantphos (0.025 mmol, 0.025 equiv), and K_3PO_4 (1.1 mmol, 1.1 equiv). If the allylic carbonate was a solid, it was added at this point. The flask was sealed with a septum and evacuated/backfilled with Ar (3 cycles). Then, dioxane (3.3 mL) and the allylic carbonate (1.5 mmol, 1.5 equiv) were added sequentially using a syringe. The reaction was heated in an oil bath to 80 °C with vigorous stirring. After 3 h, the reaction was cooled to rt, diluted with EtOAc (∼40 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL) and dried over Na_2SO_4. 1,3,5-Trimethoxybenzene (168.2 mg, 1 equiv) was added and the solution was concentrated and analyzed by ^{1}H NMR to obtain an NMR yield of the allylation step.

The crude reaction mixture was then dissolved in THF (∼4 mL) and 2 M $HCl_{(aq)}$ (4 mL) was added. The reaction mixture was stirred at rt and hydrolysis of the iminoquinone product was monitored by TLC. After ∼2−3 h, the reaction was diluted with THF (15 mL) and transferred to a separatory funnel using diethyl ether (20 mL) and water (∼5 mL) to rinse the flask. The organic phase was washed with 1 M $HCl_{(aq)}$ (4 × 5 mL). The combined aqueous phases were basified with 3 M $NaOH_{(aq)}$ (pH > 10) and extracted with dichloromethane (4 × 30 mL). The combined organic phase was dried over Na_2SO_4 and concentrated. Column chromatography (1−10% MeOH in dichloromethane) afforded the cinnamyl-derived homoallylic amine.

Preparation of 1-(4-Fluorophenyl)but-3-en-1-amine (7a). Following General Procedure F, *N*-(aryloxy)imine **3a** (327.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 141.4 mg (86%) of homoallylic amine **7a** as a yellowish oil (87% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.24 (m, 2H), 7.00 (m, 2H), 5.80−5.65 (m, 1H), 5.16−5.04 (m, 2H), 3.99 (dd, J = 8.0, 5.4 Hz, 1H), 2.48−2.26 (m, 2H), 1.61 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.9 (d, J = 244.6 Hz), 141.5 (d, J = 3.0 Hz), 135.3, 128.0 (d, J = 8.0 Hz), 118.0, 115.3 (d, J = 21.2 Hz), 54.8, 44.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.1. Spectral data are in accordance with published values.[36]

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Preparation of 1-(4-Chlorophenyl)but-3-en-1-amine (7b). Following General Procedure F, *N*-(aryloxy)imine **3b** (343.9 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 144.2 mg (79%) of homoallylic amine **7b** as a yellow oil (90% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 1.5 Hz, 4H), 5.72 (dddd, J = 16.8, 10.2, 7.9, 6.3 Hz, 1H), 5.15−5.06 (m, 2H), 3.98 (dd, J = 8.0, 5.3 Hz, 1H), 2.47−2.27 (m, 2H), 1.57 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 144.2, 135.0, 132.6, 128.5, 127.8, 118.0, 54.8, 44.1. Spectral data are in accordance with published values.[37]

Preparation of 1-(4-Bromophenyl)but-3-en-1-amine (7c). Following General Procedure F, *N*-(aryloxy)imine **3c** (388.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 139.8 mg (62%) of homoallylic amine **7c** as a yellow oil (70% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.41 (m, 2H), 7.25−7.19 (m, 2H), 5.72 (dddd, J = 16.8, 10.2, 7.9, 6.3 Hz, 1H), 5.15−5.06 (m, 2H), 3.97 (dd, J = 8.0, 5.4 Hz, 1H), 2.47−2.26 (m, 2H), 1.56 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 144.8, 135.0, 131.5, 128.2, 120.7, 118.1, 54.8, 44.2. Spectral data are in accordance with published values.[37]

Preparation of 1-(Phenyl)but-3-en-1-amine (7d). Following General Procedure F, *N*-(aryloxy)imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 128 mg (87%) of homoallylic amine **7d** as a yellow oil (89% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.31 (m, 4H), 7.27−7.22 (m, 1H), 5.76 (dddd, J = 17.1, 10.1, 8.0, 6.3 Hz, 1H), 5.25−4.99 (m, 2H), 4.00 (dd, J = 8.1, 5.3 Hz, 1H), 2.55−2.43 (m, 1H), 2.36 (dtt, J = 13.8, 8.0, 1.1 Hz, 1H), 1.54 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.0, 135.6, 128.6, 127.1, 126.4, 117.8, 55.5, 44.3. Spectral data are in accordance with published values.[38]

Preparation of 1-(4-Trifluoromethylphenyl)but-3-en-1-amine (7e). Following General Procedure F, *N*-(aryloxy)imine **3e** (377.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 2 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 149.7 mg (70%) of homoallylic amine **7e** as a yellow oil (91% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 5.73 (dddd, J = 16.7, 10.1, 8.0, 6.3 Hz, 1H), 5.17−5.08 (m, 2H), 4.08 (t, J = 6.7 Hz, 1H), 2.51−2.31 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 149.8, 134.7, 129.3 (q, J = 32.6 Hz), 126.8, 125.4 (q, J = 3.7 Hz), 123.16 (q, J = 271.8 Hz), 118.3, 55.0, 44.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.4. Spectral data are in accordance with published values.[38]

Preparation of 1-(2,6-Difluorophenyl)but-3-en-1-amine (7f). Following General Procedure H, *N*-(aryloxy)imine **3f** (345.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 2.5 h afforded, after hydrolysis and column chromatography (1−5% MeOH in dichloromethane), 127.7 mg (70%) of homoallylic amine **7f** as a yellowish oil (83% NMR yield before hydrolysis). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.89 (dd, J = 6.8, 2.9 Hz, 2H), 7.46 (dd, J = 4.9, 1.9 Hz, 3H), 7.13 (s, 2H), 5.19 (s, 1H), 1.48 (s, 18H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.2 (dd, J = 246.3, 9.1 Hz), 135.2, 128.4 (t, J = 10.8 Hz), 121.2, 117.7, 113.0−110.32 (dd, J = 20.9, 5.7 Hz), 47.3, 42.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.0. Spectral data are in accordance with published values.[39]

Preparation of 1-(3-Methylphenyl)but-3-en-1-amine (7g). Following General Procedure F, *N*-(aryloxy)imine **3g** (323.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 6 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 78.2 mg (48%) of homoallylic amine **7g** as a red oil (62% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (t, J = 7.5 Hz, 1H), 7.18−7.11 (m, 2H), 7.06 (ddt, J = 7.4, 1.9, 0.9 Hz, 1H), 5.75 (dddd, J = 16.6, 10.1, 8.0, 6.2 Hz, 1H), 5.18−5.04 (m, 2H), 3.97 (dd, J = 8.1, 5.4 Hz, 1H), 2.52−2.32 (m, 5H), 2.13 (d, J = 55.0 Hz, 2H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.4, 138.1, 135.4, 128.4, 127.8, 127.1, 123.4, 117.7, 55.4, 43.9, 21.5. FTIR: 3370, 3294, 3074, 3023, 2976, 2920, 1639, 1210, 704 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{11}H_{13}]^+$, 145.1017; found, 145.1022.

Preparation of 1-(3-Methoxyphenyl)but-3-en-1-amine (7h). Following General Procedure F, *N*-(aryloxy)imine **3h** (339.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 141.8 mg (80%) of homoallylic amine **7h** as a yellowish oil (89% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.20 (m, 1H), 6.93−6.89 (m, 2H), 6.82−6.74 (m, 1H), 5.75 (dddd, J = 17.1, 10.1, 7.9, 6.2 Hz, 1H), 5.30−4.98 (m, 2H), 3.97 (dd, J = 8.1, 5.3 Hz, 1H), 3.81 (s, 3H), 2.54−2.41 (m, 1H), 2.41−2.27 (m, 1H), 1.67 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.9, 147.7, 135.5, 129.5, 118.8, 117.8, 112.5, 112.0, 55.5, 55.3, 44.2. FTIR: 3381, 2959, 1490, 1436, 1045 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{11}H_{13}O]^+$, 161.0966; found, 161.0964.

Preparation of 1-(2,4-Dimethoxyphenyl)but-3-en-1-amine (7i). Following General Procedure F, *N*-(aryloxy)imine **3i** (369.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 150.2 mg (72%) of homoallylic amine **7i** as a light yellow oil (86% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.17 (m, 1H), 6.50−6.42 (m, 2H), 5.78 (dddd, J = 16.7, 10.1, 7.8, 6.3 Hz, 1H), 5.19−5.05 (m, 1H), 5.09−5.00 (m, 1H), 4.18 (dd, J = 8.1, 5.3 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.57−2.45 (m, 1H), 2.41−2.30 (m, 1H), 1.57 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.7, 157.9, 136.5, 127.3, 126.6, 117.1, 103.9, 98.8, 55.5, 55.4, 49.8, 42.2. FTIR: 3363, 2939, 1509, 1465, 1034 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{12}H_{15}O_2]^+$, 191.1072; found, 191.1080.

Preparation of 1-(3,4,5-Trimethoxyphenyl)but-3-en-1-amine (7j). Following General Procedure F, *N*-(aryloxy)imine **3j** (399.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 6 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 198.8 mg (83%) of homoallylic amine **7j** as a dark yellow oil (84% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (s, 2H), 5.77 (dddd, J = 17.1, 10.1, 8.2, 6.0 Hz, 1H), 5.19−5.07 (m, 2H), 3.94 (dd, J = 8.4, 5.0 Hz, 1H), 3.87 (s, 6H), 3.83 (s, 3H), 2.45 (dddt, J = 13.9, 6.3, 4.9, 1.5 Hz, 1H), 2.37−2.27 (m, 1H), 1.51 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.2, 141.7, 136.8, 135.5, 117.8, 103.1, 60.8, 56.1, 55.6, 44.4. FTIR: 3365, 3300, 3074, 2996, 2937, 1640, 1461, 1128, 918 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{13}H_{17}O_3]^+$, 221.1178; found, 221.1181.

Preparation of 1-(Naphthalene-1-yl)but-3-en-1-amine (7k). Following General Procedure F, *N*-(aryloxy)imine **3k** (359.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10

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equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 6 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 127 mg (64%) of homoallylic amine **7k** as a yellow oil (75% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.6 Hz, 1H), 7.89 (dd, J = 7.9, 1.6 Hz, 1H), 7.77 (dt, J = 8.2, 1.0 Hz, 1H), 7.67 (dt, J = 7.3, 0.9 Hz, 1H), 7.58−7.46 (m, 3H), 5.88 (dddd, J = 16.8, 10.1, 7.9, 6.4 Hz, 1H), 5.26−5.11 (m, 2H), 4.87 (dd, J = 8.4, 4.3 Hz, 1H), 2.73 (dddt, J = 12.1, 5.9, 4.3, 1.4 Hz, 1H), 2.53−2.42 (m, 1H), 1.71 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.4, 135.6, 133.9, 130.8, 129.0, 127.4, 126.0, 125.6, 125.4, 122.8, 122.5, 117.8, 50.3, 43.2. Spectral data are in accordance with published values.[40]

Preparation of 1-(2,3-Dihydrobenzofuran-5-yl)but-3-en-1-amine (7l). Following General Procedure F, *N*-(aryloxy)imine **3l** (351.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 2 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 107.4 mg (57%) of homoallylic amine **7l** as a yellowish oil (65% NMR yield before hydrolysis). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (s, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.74 (ddt, J = 17.3, 9.1, 7.0 Hz, 1H), 5.12 (d, J = 17.1 Hz, 1H), 5.07 (d, J = 10.1 Hz, 1H), 4.56 (td, J = 8.7, 1.4 Hz, 2H), 3.95−3.90 (m, 1H), 3.19 (t, J = 8.7 Hz, 2H), 2.43 (dt, J = 12.6, 5.8 Hz, 1H), 2.33 (dt, J = 14.5, 8.2 Hz, 1H), 1.64 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 159.2, 138.1, 135.8, 127.2, 126.2, 123.0, 117.6, 109.0, 71.4, 55.2, 44.5, 29.9. FTIR: 3360, 2941, 1461, 1128 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{12}H_{13}O]^+$, 173.0966; found, 173.0960.

Preparation of 1-(Benzo[*d*][1,3]dioxol-5-yl)but-3-en-1-amine (7m). Following General Procedure F, *N*-(aryloxy)imine **3m** (353.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 105.8 mg (55%) of homoallylic amine **7m** as a yellowish oil (71% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, J = 1.6 Hz, 1H), 6.81−6.72 (m, 2H), 5.93 (s, 1H), 5.79−5.66 (m, 1H), 5.15−5.03 (m, 2H), 3.92 (dd, J = 8.0, 5.5 Hz, 1H), 2.49−2.36 (m, 1H), 2.31 (dtt, J = 13.9, 8.0, 1.1 Hz, 1H), 1.58 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 147.8, 146.5, 140.1, 135.5, 119.6, 117.8, 108.2, 106.9, 101.0, 55.3, 44.4. FTIR: 3370, 3074, 2899, 1490, 1443, 1042, 917 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{11}H_{11}O_2]^+$, 175.0759; found, 175.0760.

Preparation of 1-(Thiophen-2-yl)but-3-en-1-amine (7n). Following General Procedure F, *N*-(aryloxy)imine **3n** (315.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 90 °C for 1 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 77.5 mg (51%) of homoallylic amine **7n** as a yellow oil (69% NMR yield before hydrolysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (dt, J = 3.5, 1.8 Hz, 1H), 6.98−6.92 (m, 2H), 5.78 (dddd, J = 16.8, 10.1, 7.8, 6.4 Hz, 1H), 5.20−5.09 (m, 2H), 4.29 (dd, J = 7.8, 5.4 Hz, 1H), 2.59 (dddt, J = 13.2, 6.6, 5.3, 1.4 Hz, 1H), 2.51−2.32 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 150.0, 134.6, 126.6, 123.8, 123.1, 118.4, 51.2, 44.4. Spectral data are in accordance with published values.[40]

Preparation of (2-((2-(1-Aminobut-3-en-1-yl)phenyl)thio)-phenyl)methanol (3o) and 1-(2-((2-((Allyloxy)methyl)phenyl)-thio)phenyl)but-3-en-1-amine (3o′). Following General Procedure H, *N*-(aryloxy)imine **3o** (447.6 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), allyl *tert*-butyl carbonate (237 mg, 1.5 mmol, 1.5 equiv), and dioxane (5 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 129.3 mg (45%) of **7o** as a light brown oil and 114.6 mg (35%) of diallylated amine **7o′** as a light orange oil (NMR yields were not obtained because of heavy peak overlap). Spectral data for **7o**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 7.29−7.24 (m, 1H), 7.25−7.17 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 5.80−5.70 (m, 1H), 5.16−5.03 (m, 2H), 4.74 (s, 2H), 4.55 (dd, J = 8.6, 4.8 Hz, 1H), 2.51 (dt, J = 13.5, 5.6 Hz, 1H), 2.33 (dt, J = 14.1, 8.2 Hz, 1H), 1.94 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 145.6, 141.8, 135.4, 133.6, 133.4, 132.9, 131.8, 128.8, 128.6, 128.1, 127.9, 127.9, 126.6, 118.1, 63.5, 51.7, 42.8. FTIR: 3362, 2956, 1462, 1241, 1128 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{16}H_{14}Cl]^+$, 241.0784; found, 241.0782. Spectral data for **7o′**: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 7.8 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.31−7.24 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.16−7.06 (m, 3H), 5.96 (ddt, J = 16.3, 10.7, 5.6 Hz, 1H), 5.80−5.70 (m, 1H), 5.31 (dt, J = 17.2, 1.6 Hz, 1H), 5.20 (dt, J = 10.4, 1.5 Hz, 1H), 5.14−5.04 (m, 2H), 4.64 (s, 2H), 4.55 (dd, J = 8.6, 4.6 Hz, 1H), 4.07 (dd, J = 5.6, 1.5 Hz, 2H), 2.54−2.44 (m, 1H), 2.31 (dd, J = 15.1, 7.0 Hz, 1H), 1.57 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 146.4, 138.8, 135.6, 134.8, 134.5, 133.2, 132.5, 131.8, 128.7, 128.5, 127.96, 127.8, 127.4, 126.7, 117.9, 117.4, 71.7, 70.1, 51.7, 43.0. FTIR: 3356, 2956, 2989, 1465, 1245, cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{20}H_{24}NOS]^+$, 326.1579; found, 326.1586.

Preparation of (*E*)-4-Phenyl-1-phenylbut-3-en-1-amine (7p). Following General Procedure G, *N*-(aryloxy)imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), *tert*-butyl cinnamyl carbonate (351.4 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 90 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 159.7 mg (72%) of homoallylic amine **7p** as a light brown solid (86% NMR yield before hydrolysis, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.18 (m, 11H), 6.56−6.46 (m, 1H), 6.17 (ddd, J = 15.8, 8.2, 6.5 Hz, 1H), 4.12−4.04 (m, 1H), 2.80−2.47 (m, 2H), 1.62 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.9, 137.4, 132.9, 128.6, 128.5, 127.2, 127.0, 126.4, 126.1, 55.8, 43.5. Spectral data are in accordance with published values.[41]

Preparation of (*E*)-4-(4-Fluorophenyl)-1-phenylbut-3-en-1-amine (7q). Following General Procedure G, to *N*-(aryloxy)imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl (3-(4-fluorophenyl)allyl) carbonate (378 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 2 h afforded, after hydrolysis and column chromatography (0−6% MeOH in dichloromethane), 166 mg (69%) of homoallylic amine **7q** as a yellowish solid (74% NMR yield before hydrolysis, E/Z = 6.8:1.0). mp 63−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.22 (m, 4H), 7.17 (ddd, J = 10.3, 6.1, 3.1 Hz, 3H), 6.97−6.79 (m, 2H), 6.40−6.25 (m, 1H), 5.96 (ddd, J = 15.8, 8.1, 6.5 Hz, 1H), 3.96 (dd, J = 8.0, 5.3 Hz, 1H), 2.54−2.45 (m, 1H), 2.40 (dtd, J = 13.8, 8.0, 1.2 Hz, 1H), 1.53 (s, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 163.4, 160.9, 145.9, 133.6, 133.6, 131.7, 128.6, 127.7, 127.6, 127.2, 126.9, 126.9, 126.4, 115.6, 115.4, 55.90, 43.49. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.2. FTIR: 3561, 3059, 2936, 2834, 1465, 1379,969, 763 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{16}H_{14}F]^+$, 225.1080; found, 225.1089.

Preparation of (*E*)-4-(4-Chlorophenyl)-1-phenylbut-3-en-1-amine (7r). Following General Procedure G, *N*-(aryloxy)imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl-(3-(4-chlorophenyl)allyl) carbonate (403.1 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 152.8 mg (59%) of homoallylic amine **7r** as a brown solid (86% NMR yield before hydrolysis, E/Z = 11.3:1.0). mp 68−71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.22 (m, 10H), 6.44 (dd, J = 15.9, 1.6 Hz, 1H), 6.15 (ddd, J = 15.4, 8.1, 6.6 Hz, 1H), 4.09 (dd, J = 8.0, 5.3 Hz, 1H), 2.68−2.48 (m, 2H), 1.67 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.7, 135.9, 132.8, 131.6, 128.7, 128.6, 127.9, 127.4, 127.2, 126.3, 55.8, 43.4. FTIR: 3368, 3291, 3082, 3060, 3026, 2924, 1633, 1452, 1211, 844, 829, 700 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{16}H_{14}Cl]^+$, 241.0784; found, 241.0782.

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Preparation of (*E*)-4-(4-Nitrophenyl)-1-phenylbut-3-en-1-amine (7s). Following General Procedure G, *N*-(aryloxy)imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl-(3-(4-nitrophenyl)allyl) carbonate (418.9 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 196.9 mg (73%) of homoallylic amine **7s** as a dark brown solid (98% NMR yield before hydrolysis, *E*/*Z* = 5.5:1.0). mp 79−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.02 (m, 2H), 7.35−7.30 (m, 2H), 7.29−7.14 (m, 7H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.27 (ddd, *J* = 15.8, 7.8, 6.6 Hz, 1H), 4.02 (dd, *J* = 7.7, 5.6 Hz, 1H), 2.63−2.45 (m, 2H), 1.54 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.7, 145.5, 143.8, 132.6, 130.9, 129.4, 128.6, 127.3, 126.6, 126.3, 126.2, 124.0, 123.5, 77.3, 55.8, 43.5. FTIR: 3369, 3307, 3057, 3022, 2932, 2903, 1688, 1512, 1344, 971, 802, 703 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{16}H_{14}NO_2]^+$, 252.1025; found, 252.1019.

Preparation of (*E*)-4-(3-(Trifluoromethyl)phenyl)-1-phenylbut-3-en-1-amine (7t). Following General Procedure G, *N*-(aryloxy)imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl-(3-(3-(trifluoromethyl)phenyl)allyl) carbonate (453.5 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 220.9 mg (76%) of homoallylic amine **7t** as light yellow oil (77% NMR yield before hydrolysis, *E*/*Z* = 4.5:1.0). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.35 (dd, *J* = 12.9, 7.5 Hz, 2H), 7.31−7.20 (m, 5H), 7.19−7.12 (m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.14 (ddd, *J* = 15.3, 8.0, 6.6 Hz, 1H), 3.99 (dd, *J* = 7.9, 5.3 Hz, 1H), 2.53 (dt, *J* = 12.1, 5.1 Hz, 1H), 2.44 (dt, *J* = 14.2, 7.9 Hz, 1H), 1.64 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.7, 138.3, 131.6, 130.6 (q, *J* = 151.6 Hz), 129.4, 129.3, 129.1, 128.7, 127.3, 126.4, 124.3 (q, *J* = 273.0 Hz), 123.8 (q, *J* = 4.0 Hz), 122.9 (q, *J* = 3.8 Hz), 55.9, 43.5. FTIR: 3377, 3028, 2926, 1493, 1453, 1330, 1204, 967 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{17}H_{17}F_3N]^+$, 292.1313; found, 292.1326.

Preparation of (*E*)-4-(4-Methylphenyl)-1-phenylbut-3-en-1-amine (7u). Following General Procedure G, to *N*-(aryloxy)imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl-3-(4-(methylphenyl)allyl) carbonate (372.5 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (1−10% MeOH in dichloromethane), 151.9 mg (64%) of homoallylic amine **7u** as off-white solid (64% NMR yield before hydrolysis, *E*/*Z* = 18:1). mp 67−68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.34 (m, 2H), 7.38−7.31 (m, 1H), 7.29−7.20 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.10 (ddd, *J* = 15.8, 8.2, 6.5 Hz, 1H), 4.07 (dd, *J* = 8.1, 5.2 Hz, 1H), 2.65−2.56 (m, 1H), 2.50 (dtd, *J* = 13.6, 8.1, 1.2 Hz, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.9, 137.1, 134.7, 132.9, 129.4, 128.6, 127.2, 126.5, 126.2, 126.1, 56.0, 43.6, 21.3. FTIR: 3377, 3026, 2919, 1513, 1451, 702 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{17}H_{17}]^+$, 221.1330; found, 221.1340.

Preparation of (*E*)-4-(3-Methoxyphenyl)-1-phenylbut-3-en-1-amine (7v). Following General Procedure G, *N*-(aryloxy)imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), MeCN (0.52 mL, 10 mmol, 10 equiv), (*E*)-*tert*-butyl-(3-(3-methoxyphenyl)allyl) carbonate (396.5 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 90 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 185.5 mg (73%) of homoallylic amine **7v** as a yellowish oil (89% NMR yield before hydrolysis, *E*/*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42−7.33 (m, 4H), 7.32−7.19 (m, 2H), 6.96 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.90 (t, *J* = 2.1 Hz, 1H), 6.79 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.18 (ddd, *J* = 16.0, 8.2, 6.6 Hz, 1H), 4.09 (dd, *J* = 8.1, 5.2 Hz, 1H), 3.81 (s, 3H), 2.68−2.47 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 159.8, 145.8, 138.9, 132.8, 129.6, 128.6, 127.5, 127.1, 126.4, 118.8, 112.8, 111.6, 77.5, 77.2, 55.8, 55.2, 43.5. FTIR: 3557, 3292, 3059, 3026, 3002, 2936, 2834, 1465, 1379, 1209, 1153, 1044, 969, 763, 701 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{17}H_{17}O]^+$, 237.1279; found, 237.1282.

Preparation of (*E*)-4-(2,3-Dimethoxyphenyl)-1-phenylbut-3-en-1-amine (7w). Following General Procedure H, *N*-(aryloxy)-imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), (*E*)-*tert*-butyl-(3-(2,3-dimethoxyphenyl)allyl) carbonate (441.5 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 90 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 223.6 mg (79%) of homoallylic amine **7w** as a brownish oil (93% NMR yield before hydrolysis, *E*/*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40−7.30 (m, 4H), 7.29−7.21 (m, 1H), 7.06−6.95 (m, 2H), 6.82−6.73 (m, 2H), 6.17 (ddd, *J* = 15.9, 8.0, 6.7 Hz, 1H), 4.08 (dd, *J* = 7.7, 5.6 Hz, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 2.70−2.51 (m, 2H), 1.74 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 153.02, 146.3, 145.7, 131.6, 128.50, 128.49, 127.05, 127.01, 126.4, 124.0, 118.1, 110.9, 60.8, 55.9, 55.8, 43.7. FTIR: 3363, 3059, 3026, 2999, 2932, 2903, 1676, 1476, 1453, 1380, 1209, 975, 748, 701 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{18}H_{19}O_2]^+$, 267.1385; found, 267.1384.

Preparation of (*E*)-4-(Furan-2-yl)-1-phenylbut-3-en-1-amine (7x). Following General Procedure H, *N*-(aryloxy)imine **3d** (309.4 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), (*E*)-*tert*-butyl-(3-(furan-2-yl)allyl) carbonate (336.4 mg, 1.5 mmol, 1.5 equiv), and dioxane (3.3 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (2−5% MeOH in dichloromethane), 142.1 mg (67%) of homoallylic amine **7x** as a yellowish oil (96% NMR yield before hydrolysis, *E*/*Z* > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.29 (m, 5H), 7.29−7.22 (m, 2H), 6.34 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.15 (d, *J* = 3.3 Hz, 1H), 6.10 (ddd, *J* = 15.4, 8.3, 6.6 Hz, 1H), 4.06 (dd, *J* = 8.2, 5.1 Hz, 1H), 2.60 (dddd, *J* = 13.4, 6.6, 5.1, 1.5 Hz, 1H), 2.46 (dtd, *J* = 13.9, 8.2, 1.1 Hz, 1H), 1.60 (s, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 152.8, 145.8, 141.6, 128.5, 127.1, 126.3, 126.0, 121.3, 111.2, 106.8, 55.8, 43.4. FTIR: 3365, 3298, 3148, 3083, 3060, 3027, 2902, 1677, 1452, 962, 761, 701 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{14}H_{13}O]^+$, 197.0966; found, 197.0961.

Preparation of (*E*)-1-Phenylpent-3-en-1-amine (Linear 7y) and 2-Methyl-1-phenylbut-3-en-1-amine (Branched 7y). Following General Procedure H, *N*-(aryloxy)imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), (*E*)-but-2-en-1-yl *tert*-butyl carbonate (354.4 mg, 2.0 mmol, 2.0 equiv), and dioxane (2.5 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (0−3% MeOH in dichloromethane), 75.8 mg (47%) of **7y** as a yellowish oil and as a mixture of linear and branched (5.4:1.0 ratio) isomers. (Branched isomer dr = 4:1). Mixture of isomers linear/anti-branched/syn-branched = 1.0:0.16:0.04 (60% NMR yield before hydrolysis, linear/branched = 5.9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 4.1, 3.3 Hz, 4.6 H), 7.27−7.21 (m, 1.7H), 5.74 (ddd, *J* = 17.2, 10.3, 8.4 Hz, 0.16H), 5.69−5.63 (m, 0.04H), 5.61−5.49 (m, 1H), 5.38 (dddd, *J* = 15.3, 7.9, 6.2, 1.6 Hz, 1H), 5.17 (ddd, *J* = 17.1, 1.9, 0.9 Hz, 0.16H), 5.11 (ddd, *J* = 10.3, 1.9, 0.6 Hz, 0.16H), 5.07−4.98 (m, 0.08H), 3.94 (dd, *J* = 8.3, 5.1 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, 0.04H), 3.64 (d, *J* = 8.4 Hz, 0.16H), 2.50 (m, 0.04H), 2.44−2.33 (m, 1.19H), 2.32−2.22 (m, 1.04H), 1.67 (dd, *J* = 6.4, 1.2 Hz, 3H), 1.64 (s, 2.4H), 0.98 (d, *J* = 6.8 Hz, 0.12H), 0.82 (d, *J* = 6.8 Hz, 0.48H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.1, 128.54, 128.50, 127.9, 127.0, 126.5, 55.8, 43.1, 18.2. Spectral data are in accordance with published values.[42]

Preparation of *syn*-Cyclohex-2-en-1-yl(phenyl)-methanamine (7aa). Following General Procedure H, *N*-(aryloxy)-imine **3d** (309.5 mg, 1 mmol, 1 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 0.01 equiv), K_3PO_4 (233.5 mg, 1.1 mmol, 1.1 equiv), Xantphos (14.5 mg, 0.025 mmol, 0.025 equiv), *tert*-butyl-cyclohex-2-en-1-yl carbonate (mg, 2.0 mmol, 2.0 equiv), and dioxane (2.5 mL) at 80 °C for 3 h afforded, after hydrolysis and column chromatography (0−3% MeOH in dichloromethane), 67.7 mg (36%, dr > 20:1) of **7aa** as a yellowish oil (43% NMR yield before hydrolysis). ^{1}H NMR (500

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MHz, $CDCl_3$): δ 7.33 (d, J = 4.3 Hz, 4H), 7.25 (dd, J = 9.2, 4.8 Hz, 1H), 5.79−5.62 (m, 1H), 5.38 (dd, J = 10.2, 2.6 Hz, 1H), 3.82 (d, J = 7.1 Hz, 1H), 2.46−2.34 (m, 1H), 1.97 (ddt, J = 7.8, 5.6, 2.9 Hz, 2H), 1.75 (pd, J = 7.1, 2.2 Hz, 2H), 1.62 (s, 2H), 1.56−1.40 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 144.9, 129.4, 129.3, 128.4, 127.3, 127.0, 60.3, 43.2, 25.4, 24.7, 21.7. Spectral data are in accordance with published values.[43]

Reaction Profiles. *Reaction Profile for the Reaction between N-(Aryloxy)imine **3d** and 4-Fluorocinnamyl tert-Butyl Carbonate.* To a dry, 7 mL vial were added a magnetic stir bar, *N*-(aryloxy)imine **3d** (185.7 mg, 0.6 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 100.9 mg, 0.6 mmol, 1 equiv), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 0.01 equiv), and K_3PO_4 (140.1 mg, 0.66 mmol, 1.1 equiv). The vial was sealed and evacuated/backfilled with Ar (4 cycles). Dioxane (2 mL), MeCN (0.31 mL, 6 mmol, 10 equiv), and 4-fluorocinnamyl *tert*-butyl carbonate (227.1 mg, 0.9 mmol, 1.5 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (∼0.1 mL) were taken over time, diluted with EtOAc (∼1 mL) and hexanes (∼1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H and ^{19}F NMR.

*Reaction Profile for the Reaction between N-(Aryloxy)imine **3d** and Crotyl tert-Butyl Carbonate.* To a dry, 7 mL vial were added a magnetic stir bar, *N*-(aryloxy)imine **3d** (123.8 mg, 0.4 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 67.3 mg, 0.4 mmol, 1 equiv), $Pd_2(dba)_3$ (3.7 mg, 0.004 mmol, 0.01 equiv), Xantphos (5.8 mg, 0.01 mmol, 0.025 equiv), and K_3PO_4 (93.4 mg, 0.44 mmol, 1.1 equiv). The vial sealed and evacuated/backfilled with Ar (4 cycles). Dioxane (1 mL) and crotyl *tert*-butyl carbonate (142 mg, 0.8 mmol, 2 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (∼0.1 mL) were taken over time, diluted with EtOAc (∼1 mL) and hexanes (∼1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

*Reaction Profile for the Reaction between N-(Aryloxy)imine **3d** and Allyl tert-Butyl Carbonate.* To a dry, 7 mL vial were added a magnetic stir bar, *N*-(aryloxy)imine **3d** (154.8 mg, 0.5 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 84.1 mg, 0.5 mmol, 1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.01 equiv), and K_3PO_4 (116.7 mg, 0.55 mmol, 1.1 equiv). The vial was sealed and evacuated/backfilled with Ar (4 cycles). Dioxane (2.5 mL), MeCN (0.26 mL, 5 mmol, 10 equiv), and crotyl *tert*-butyl carbonate (118.7 mg, 0.75 mmol, 1.5 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (∼0.1 mL) were taken over time, diluted with EtOAc (∼1 mL) and hexanes (∼1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

Preparation of Imines *C3-iso*-6q, *C3-iso*-6y, and *C3-iso*-6d. *Preparation of 4-(((E)-Benzylidene)amino)-2,6-di-tert-butyl-4-((E)-3-(4-fluorophenyl)allyl)cyclohexa-2,5-dien-1-one (**C3-iso-6q**).* To a 25 mL round bottom flask were added a stir bar, *N*-(aryloxy)imine **3d** (900 mg, 2.91 mmol, 1 equiv), K_3PO_4 (679 mg, 3.2 mmol, 1.1 equiv), and $Pd_2(dba)_3$ (53 mg, 0.058 mmol, 0.02 equiv). The flask was evacuated/backfilled with Ar (3 cycles). MeCN (2.9 mL), THF (2.9 mL), and 4-fluorocinnamyl *tert*-butyl carbonate (868 mg, 3.44 mmol, 1.18 equiv) were added sequentially using a syringe. The reaction was heated in an oil bath to 55 °C. After 3 h, the reaction was cooled to rt, opened to air, diluted with EtOAc (50 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The product was purified by column chromatography on buffered silica gel: first column (5% EtOAc in hexanes, 1% Et_3N) and second column (4−10% Et_2O in hexanes, 1% Et_3N), followed by recrystallization from hexanes at −20 °C, afforded 105 mg (8%) of imine ***C3-iso*-6q** as white crystals. X-ray crystallography data were obtained, see Supporting Information. mp 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.78 (dd, J = 7.6, 2.0 Hz, 2H), 7.50−7.39 (m, 3H), 7.23−7.11 (m, 2H), 6.95 (t, J = 8.7 Hz, 2H), 6.64 (s, 2H), 6.35 (d, J = 15.8 Hz, 1H), 5.96 (dt, J = 15.4, 7.4 Hz, 1H), 2.82 (dd, J = 7.5, 1.3 Hz, 2H), 1.23 (s, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 186.9, 162.3 (d, J = 246.2 Hz), 160.8, 147.8, 142.0, 136.4, 133.5 (d, J = 3.6 Hz), 133.0, 131.3, 128.8, 128.5, 127.7 (d, J = 7.9 Hz), 124.2 (d, J = 2.5 Hz), 115.6 (d, J = 21.2 Hz), 65.0, 45.5, 35.2, 29.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.0. FTIR: 3029, 2970, 1663, 1640 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{30}H_{35}FNO]^+$, 444.2703; found, 444.2703.

*Preparation of 4-(((E)-Benzylidene)amino)-4-((E)-but-2-en-1-yl)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**C3-iso-6y**).* To a 25 mL round bottom flask were added a stir bar and *N*-(aryloxy)imine **3d** (800 mg, 2.59 mmol, 1 equiv). The flask was evacuated/backfilled with Ar (3 cycles). MeCN (12 mL) was added using a syringe, followed by a solution of *t*-BuOK (1 M in THF, 2.8 mL, 1.1 equiv). After 15 min, crotyl bromide (85% w/w, 0.47 mL, 3.88 mmol, 1.5 equiv) was added dropwise. After 2 h, the reaction was opened to air, diluted with EtOAc (40 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The product was purified by column chromatography on buffered silica gel (4% EtOAc in hexanes, 1% Et_3N) and afforded 124 mg (13%) of imine ***C3-iso*-6y** as a yellowish semisolid. mp 61−63 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.79−7.63 (m, 2H), 7.47−7.40 (m, 3H), 6.58 (s, 2H), 5.50−5.37 (m, 1H), 5.33−5.18 (m, 1H), 2.60 (dd, J = 7.3, 1.2 Hz, 2H), 1.61 (dd, J = 6.4, 1.5 Hz, 3H), 1.25 (s, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 187.0, 160.4, 147.4, 142.3, 136.5, 131.2, 129.9, 128.8, 128.4, 125.0, 64.9, 45.1, 35.1, 29.8. FTIR: 2958, 2917, 2870, 1661, 1639, 1364 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{25}H_{34}Cl]^+$, 364.2640; found, 364.2643.

*Preparation of (E)-4-Allyl-4-(benzylideneamino)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (**C3-iso-6d**).* To a 25 mL round bottom flask were added a stir bar and *N*-(aryloxy)imine **3d** (470 mg, 1.52 mmol, 1 equiv). The flask was evacuated/backfilled with Ar (3 cycles). MeCN (12 mL) was added using a syringe, followed by a solution of *t*-BuOK (1 M in THF, 1.7 mL, 1.1 equiv). After 15 min, allyl bromide (0.2 mL, 2.28 mmol, 1.5 equiv) was added dropwise. After 2 h, the reaction was opened to air, diluted with EtOAc (40 mL), transferred to a separatory funnel, and washed with $NH_4Cl_{(sat)}$ (5 mL). The aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The product was purified by column chromatography on buffered silica gel: first column (30−40% dichloromethane in hexanes, 1% Et_3N) and second column (2% EtOAc in hexanes, 1% Et_3N) afforded 475 mg (89%) of imine ***C3-iso*-6d** as a yellowish semisolid. mp 40−42 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.75 (dd, J = 7.3, 2.0 Hz, 2H), 7.43 (d, J = 7.1 Hz, 3H), 6.60 (s, 2H), 5.69 (ddt, J = 17.4, 10.3, 7.3 Hz, 1H), 5.28−4.94 (m, 2H), 2.80−2.59 (m, 2H), 1.25 (s, 18H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 187.0, 160.6, 147.5, 142.1, 136.4, 132.9, 131.3, 128.8, 128.4, 118.9, 64.2, 46.4, 35.2, 29.8. FTIR: 2955, 2870, 1661, 1637, 1364 cm^{-1}. HRMS (ESI) *m*/*z*: calcd for $[C_{24}H_{32}NO]^+$, 350.2484; found, 350.2486.

Isomerization Studies of Imines *C3-iso*-6. *Isomerization of **C3-iso-6q** in the Presence of Pd.* To a dry, 7 mL vial were added a magnetic stir bar, imine ***C3-iso*-6q** (40 mg, 0.09 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 15.2 mg, 0.09 mmol, 1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.01 equiv), and K_3PO_4 (21.1 mg, 0.099 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (4 cycles). Dioxane (0.3 mL) and MeCN (47 μL, 5 mmol, 10 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (∼0.1 mL) were taken at 1.3 and 3 h, diluted with EtOAc (∼1 mL) and hexanes (∼1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

*Isomerization of **C3-iso-6q** in the Absence of Pd.* To a dry, 7 mL vial were added a magnetic stir bar, imine ***C3-iso*-6q** (40 mg, 0.09 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 15.2 mg, 0.09 mmol, 1 equiv), and K_3PO_4 (21.1 mg, 0.099 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (4 cycles). Dioxane (0.3 mL) and MeCN (47 μL, 5 mmol, 10 equiv)

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were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (~0.1 mL) were taken at 1.3 and 3 h, diluted with EtOAc (~1 mL) and hexanes (~1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

*Isomerization of **C3-iso-6y** in the Presence of Pd.* To a dry, 7 mL vial were added a magnetic stir bar, imine ***C3-iso-6y*** (40 mg, 0.11 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 18.5 mg, 0.11 mmol, 1 equiv), $Pd_2(dba)_3$ (1 mg, 0.0011 mmol, 0.01 equiv), Xantphos (1.6 mg, 0.0028 mmol, 0.025 equiv), and K_3PO_4 (25.7 mg, 0.121 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (4 cycles). Dioxane (0.3 mL) was added using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (~0.1 mL) were taken at 1, 2, and 3 h, diluted with EtOAc (~1 mL) and hexanes (~1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR. Complete conversion was observed after 1 h and no further changes were observed at 2 and 3 h.

*Isomerization of **C3-iso-6y** in the Absence of Pd.* To a dry, 7 mL vial were added a magnetic stir bar, imine ***C3-iso-6y*** (40 mg, 0.11 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 18.5 mg, 0.11 mmol, 1 equiv), Xantphos (1.6 mg, 0.0028 mmol, 0.025 equiv), and K_3PO_4 (25.7 mg, 0.121 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (4 cycles). Dioxane (0.3 mL) was added using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (~0.1 mL) were taken at 1, 2, and 3 h, diluted with EtOAc (~1 mL) and hexanes (~1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

*Isomerization of **C3-iso-6d** in the Presence of Pd.* To a dry, 7 mL vial were added a magnetic stir bar, imine ***C3-iso-6d*** (62 mg, 0.177 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 29.8 mg, 0.177 mmol, 1 equiv), $Pd_2(dba)_3$ (1.6 mg, 0.0018 mmol, 0.01 equiv), and K_3PO_4 (41.4 mg, 0.195 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (4 cycles). Dioxane (0.9 mL) and MeCN (92 μL, 1.77 mmol, 10 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (~0.1 mL) were taken at 1, 2, and 3 h, diluted with EtOAc (~1 mL) and hexanes (~1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

*Isomerization of **C3-iso-6d** in the Absence of Pd.* To a dry, 7 mL vial was added a magnetic stir bar, imine ***C3-iso-6d*** (62 mg, 0.177 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 29.8 mg, 0.09 mmol, 1 equiv), and K_3PO_4 (41.4 mg, 0.195 mmol, 1.1 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (four cycles). Dioxane (0.9 mL) and MeCN (92 μL, 1.77 mmol, 10 equiv) were added sequentially using a syringe. The reaction was heated in an aluminum block to 80 °C with vigorous stirring. Aliquots (~0.1 mL) were taken at 1, 2, and 3 h, diluted with EtOAc (~1 mL) and hexanes (~1 mL), washed with $NH_4Cl_{(sat)}$, concentrated, and analyzed by ^1H NMR.

TEMPO-Trapping Experiments. *Preparation of (E)-1-((3-(4-Fluorophenyl)allyl)oxy)-2,2,6,6-tetramethylpiperidine (**14q**).* To a dry, 7 mL vial was added a magnetic stir bar, imine ***C3-iso-6q*** (11.3 mg, 0.025 mmol, 1 equiv), and TEMPO (6 mg, 0.038 mmol, 1.5 equiv). The vial was capped, sealed, and evacuated/backfilled with Ar (3 cycles). Dioxane (0.13 mL) was added. The reaction was heated to 80 °C in an aluminum block. After 2 h, the reaction was cooled to rt, opened to air, and concentrated. Column chromatography (10% EtOAc in hexanes) afforded 2.7 mg (37%) of **14q** as a light orange oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41−7.32 (m, 1H), 7.00 (t, J = 8.7 Hz, 1H), 6.56 (d, J = 15.9 Hz, 1H), 6.21 (dt, J = 15.8, 6.0 Hz, 1H), 4.43 (dd, J = 6.0, 1.7 Hz, 1H), 1.51−1.44 (m, 2H), 1.34 (dt, J = 12.9, 3.3 Hz, 1H), 1.26 (d, J = 12.5 Hz, 1H), 1.21 (s, 3H), 1.13 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 162.4 (d, J = 246.3 Hz), 133.3 (d, J = 3.3 Hz), 130.4, 128.1 (d, J = 8.1 Hz), 125.4 (d, J = 2.6 Hz), 115.6, 115.4, 78.1, 59.9, 39.8, 33.2, 20.4, 17.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ −114.8. FTIR: 2973, 2929, 1603, 1509, 1412 cm^{-1}. HRMS (ESI) m/z: calcd for $[C_{18}H_{27}FNO]^+$, 292.2077; found, 292.2086.

Thermal Isomerization of *C5-iso*-6bb. *Generation of **C5-iso-6bb** and Thermal Isomerization into **6bb**.* To a dry, 7 mL vial were added *N*-(aryloxy)imine **3a** (100 mg, 0.305 mmol, 1 equiv), 1,3,5-trimethoxybenzene (internal standard, 51.4 mg, 0.305 mmol, 1 equiv), and *t*-BuOK (37.7 mg, 0.336 mmol, 1.1 equiv). The vial was capped, sealed with Parafilm, and evacuated/backfilled with Ar (3 cycles). THF (0.5 mL) and MeCN (1.5 mL) were added using a syringe to give a deep red suspension. After 5 min, the reaction was cooled at 0 °C in an ice bath, briefly opened to air, and cinnamyl bromide (90.3 mg, 0.458 mmol, 1.5 equiv) was added at once. The vial was resealed and flushed with Ar. The reaction turned green in ~4 min. After 20 min, an aliquot was taken, diluted with EtOAc (1 mL) and hexanes (1 mL), washed with $NH_4Cl_{(sat)}$ (0.5 mL), concentrated, and analyzed by ^1H NMR. The reaction was warmed to rt and after 2 h, an aliquot was taken and worked up as described above. The reaction was then warmed to 65 °C in an aluminum block. After 2 h, an aliquot was taken and worked up as described above. Although ***C5-iso-6bb*** was not isolated, its chemical shifts highlighted in the three spectra (see Supporting Information) were consistent with its structure. Specifically, the methylene diastereotopic protons appeared at 3.14 (m) and 2.41 ppm (m), the chemically inequivalent vinylic protons appeared at 6.86 (d) and 5.89 (d) ppm, and the chemically inequivalent methyl protons (*tert*-butyl groups) appeared at 1.25 (s) and 1.02 (s) ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01020.

Copies of ^1H, ^{13}C, and ^{19}F NMR, crystallographic data for compound ***C3-iso-6q*** (PDF)

Accession Codes

CCDC 2036140 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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