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Substrate-Directable Heck Reactions with Arenediazonium Salts. The Regio- and Stereoselective Arylation of Allylamine Derivatives and Applications in the Synthesis of Naftifine and Abamines

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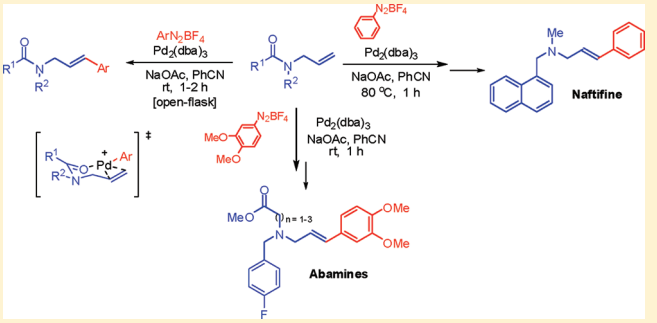
Supporting Information

ABSTRACT: The palladium-catalyzed, substrate-directable Heck−Matsuda reaction of allylamine derivatives with arenediazonium salts is reported. The reaction proceeds under mild conditions, with excellent regio- and stereochemical control as a function of coordinating groups present in the allylamine substrate. The distance between the olefin moiety and the carbonylic system seems to play a key role regarding the regiocontrol. The method presents itself as robust, as simple to carry out, and with wide synthetic scope concerning the allylic substrates and the type of arenediazonium employed. The synthetic potential of the method is illustrated by the short total syntheses of the bioactive compounds naftifine, abamine, and abamine SG.



INTRODUCTION

The Heck arylation of olefins is a powerful tool for the formation of C−C bonds.[1] The Heck reactions usually rely on aryl halides and triflates as electrophiles. An interesting alternative, which has attracted increasing attention in the past few years, is the use of arenediazonium salts (the Heck−Matsuda reaction).[1f−h] Arenediazonium salts make the Heck reactions operationally simple to carry out, faster, greener, and more economical, avoiding the use of the toxic phosphine ligands. In addition, these reactions can in several cases be carried out under base-free conditions.[2] Many of the key features of the Heck−Matsuda reactions are directly connected to the highly reactive "ligand-free" ionic arylpalladium intermediates generated in the course of these reactions.[3] Having successfully developed the palladium-catalyzed Heck reaction of allylic esters with arenediazonium salts,[4] we planned to extend our investigation to the Heck arylation of substrates bearing an allylamine moiety (such as amides, carbamates, imides, etc). When allylamines are used in standard Heck arylation, mixtures of β- and γ-aryl allylamines are usually observed.[5] In some cases, high degrees of regioselectivity can be achieved when employing bulky allylamines, thus favoring reactions at the terminus of the allylic system.[6] One of the rare studies describing the γ-arylation of allylamines was reported by Ripin et al.[7] In this case, the Heck arylation between bis-Boc allylamine and aryl iodide was the key step in the synthesis of anticancer compound CP-724,714. According to the authors, the high γ/β selectivity achieved (96/4) was due to the steric hindrance of bis-Boc substituents in the allylamine. However, most of the examples available indicate the preferential formation of the β-arylated allylamines in good to moderate yields under rather harsh conditions.[8] Very recently, we learned of a communication by Cacchi et al.,[9] which describes the Heck arylation of some allylamine derivatives using arenediazonium salts. This interesting study relies on somewhat congested allylamine derivatives, such as the *N*-bis-Boc allylamine (see Table 2, entry 4). However, the authors also reported that monosubstituted allylamine derivatives provide rather low regioselectivities for the arylated products (3:1 γ/β ratio). These last results are in sharp contrast with the results obtained by us.

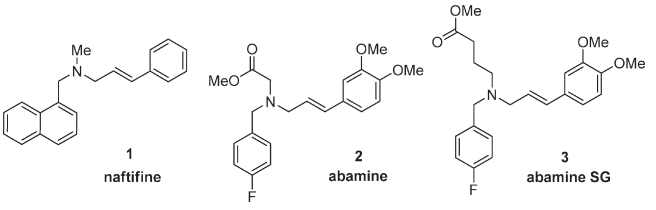


Figure 1. Structures of naftifine **1**, abamine **2**, and abamine SG **3**.

Herein, we present an operationally simple and synthetically attractive alternative for the stereo- and regioselective Heck arylation of allylamine derivatives based on the use of arenediazonium salts.[9] We also make the point that these Heck arylations are strongly influenced by the substrate itself by means of an internal chelation of the cationic "ligand-free" ArPd(II) intermediate.

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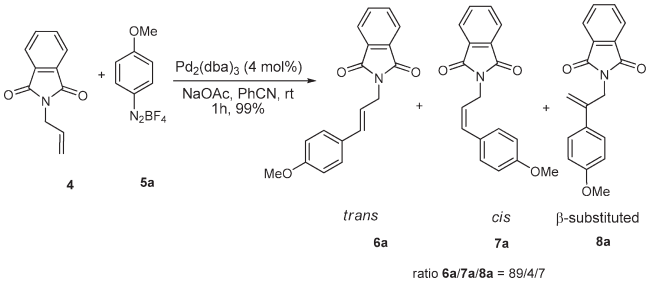
Scheme 1. Heck Arylation of Allylic Phthalimide 4a



Our results also include the application of this protocol in the total synthesis of biologically active compounds naftifine **1**, abamine **2**, and abamine SG **3** (Figure 1).

RESULTS AND DISCUSSION

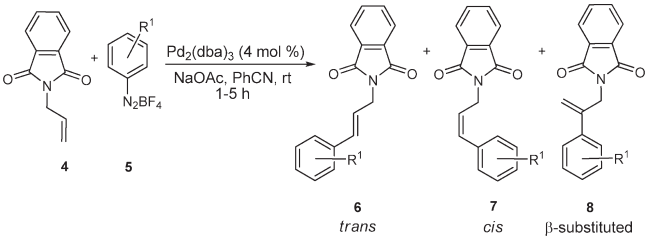
We started our investigation of the Heck arylation with the allylphthalimide **4** using the same conditions described in our recent work with allylic esters.[4] Initial reaction conditions employed allylphthalimide **4** (0.3 mmol), 4-methoxybenzene diazonium tetrafluoroborate **5a** (0.25 mmol), $Pd_2(dba)_3$ (4 mol %), and NaOAc as base, in benzonitrile, at room temperature, for 1 h. Under these conditions, the γ-arylated allylic amine was obtained in high yield, with good regio- and stereochemical control (ratio **6a**/**7a**/**8a** = 89:4:7) (Scheme 1). In this case, we observed the formation of the γ,γ-diarylated product in approximately 10%. To avoid the diarylation reaction, the phthalimide allylic **4** was used in excess (1.2 equiv), and the desired product was observed in 99% yield. Attempts at fine-tuning the reaction conditions, such as lowering the load of palladium from 4 to 2 mol % or changing the solvent from PhCN to MeCN, resulted in decreased yields.

Inspection of Table 1 shows that the reaction works well for a variety of arenediazonium salts. Both electron-rich and electron-poor arenediazonium salts provide the desired products in good to high yields and selectivity. Halogen substituents are well tolerated, and it is noteworthy that 4-iodobenzenediazonium tetrafluoroborate underwent selective oxidative addition, yielding the iodine-containing products **6h**−**8h** in high isolated yields (Table 1, entry 8). When using the bulky 2-naphthyl diazonium salt, we did not observe the formation of the *cis* isomer **7j**, with the *trans* isomer **6j** formed almost exclusively (Table 1, entry 10).

To evaluate the applicability of our system at the gram scale, the reaction between allyl phthalimide **4** and 4-fluorobenzenediazonium tetrafluoroborate was performed at the 5 mmol scale (limiting reagent was arenediazonium salt) (Scheme 2). The product was purified by flash chromatography (hexanes:ethyl acetate as eluent) to provide 1.405 g of aryl allylamine derivative **6** in 91% as a mixture of isomers (ratio **6e**/**7e**/**8e** = 96:2:2), which appears as a single spot on TLC. The mixture of isomers was then recrystallyzed in $CHCl_3$ to provide the pure *trans* isomer **6e** in 83% yield.

We next explored the generality of our method, extending the conditions to other allylamine derivatives. Following these preliminary results, we then evaluated the scope of Heck arylation with a variety of mono- and dicarbonylated allylamine compounds, as well as with a variety of arenediazonium salts. As shown in Table 2, all the expected Heck adducts were obtained in high yields and excellent selectivity, including the case of an

Table 1. Heck Arylation of Allylic Phthalimide 4 with Arenediazonium Salts 5



entry	R^1	time (h)	yield (%)[a]	ratio **6**/**7**/**8**
1	4-MeO	1	99	**6a**/**7a**/**8a** = 89:4:7
2	2-MeO	2	93	**6b**/**8b**/**8b** = 92:3:5
3	4-Cl	1	95	**6c**/**7c**/**8c** = 89:7:4
4	3,4-$(Cl)_2$	2	82	**6d**/**7d**/**8d** = 93:5:2
5[b]	4-F	4	91	**6e**/**7e**/**8e** = 95:2:3
6	3-F	1	99	**6f**/**7f**/**8f** = 92:5:3
7	4-Br	1	98	**6g**/**7g**/**8g** = 91:6:3
8	4-I	2	96	**6h**/**7h**/**8h** = 86:9:5
9	H	1	99	**6i**/**7i**/**8i** = 93:4:3
10	2-naphthyl	3	98	**6j**/**7j**/**8j** = 98:0:2
11	4-C_6H_5	5	97	**6k**/**7k**/**8k** = 92:4:4
12[c]	4-NO_2	2	86	**6l**/**7l**/**8l** = 92:6:2
13	3,4-(−OCH_2O−)	2	84	**6m**/**7m**/**8m** = 86:7:7
14	4-Me	1	95	**6n**/**7n**/**8n** = 91:4:5

[a] The reaction was carried under air, by using allylic phthalimide **4** (0.062 g, 0.3 mmol), the appropriate arenediazonium tetrafluoroborate (0.25 mmol), $Pd_2(dba)_3$·dba (4 mol %, 10 mg), sodium acetate (3 equiv, 0.75 mmol, 0.061 g), and benzonitrile (1 mL). The reaction was stirred at room temperature with the reaction progress monitored by the evolution of N_2. Yields refer to mixtures of the three isomers (a single spot on TLC). [b] Compounds **6e**, **7e**, and **8e** were separated by preparative HPLC and fully characterized. The ratio between regioisomers was based on integration of appropriate structural assignment. See Supporting Information for further details. [c] The reaction was carried out at 80 °C.

allylamine system bearing a free NH (Table 2, entry 7). In contrast, when we used *N*,*N*-dimethyl allylamine **9f**, no Heck adduct was observed. We believe that in this case the nitrogen atom of the allylamine strongly coordinates to the palladium catalyst, deactivating it.

With the monocarbonylated systems displaying good reactivity, we then investigated the Heck arylation of allylamides and allyltosylamide with different arenediazonium salts (Table 3). In all cases, the desired products were obtained in high yields for all the diazonium salts tested, including neutral, electron-rich, electron-poor, and bulky ones. Remarkably, in almost every case, the Heck reaction proceeded with very high regio- and stereochemical control in favor of the *E* isomer, except in the entries 13 and 14. Entries 13 and 14 were designed to probe the regio- and stereochemical aspects of the reaction with the common and unbulky acetyl group and with a weak coordinating group such as the trifluoroacetyl group on the nitrogen.

The proposed main catalytic cycle for the Heck arylation of the acyclic mono- and disubstituted allylamine derivatives with arenediazonium tetrafluoroborates is shown in Scheme 3. These reactions seem to rely at its initial stages on the simultaneous

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Scheme 2. Heck Arylation of Allyl Phthalimide 4 in the 5 mmol Scale

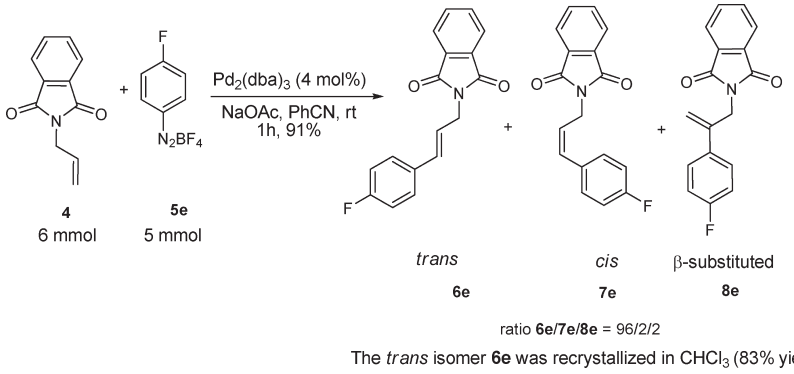
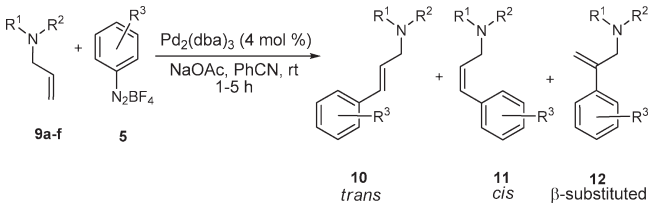


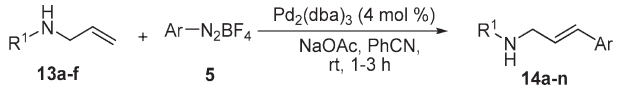
Table 2. Heck Arylation of Allylamines 9a−f



entry	R^1, R^2	R^3	yield (%)[a]	ratio **10/11/12**
1	R^1 = CO_2Me	4-OMe	93	**10a/11a/12a** = 91:5:4
	R^2 = Boc, **9**[a]			
2	R^1 =CO_2Me	4-Cl	92	**10b/11b/12b** = 93:4:3
	R^2 = Boc, **9**[a]			
3	R^1 = CO_2Me	3-Br	91	**10c/11c/12c** = 93:4:3
	R^2 = Boc, **9**[a]			
4	R^1, R^2 = Boc, **9b**	4-OMe	83	**10d/11d/12d** = 93:2:5
5	R^1 = COMe	4-OMe	98	**10e/11e/12e** = 92:3:5
	R^2 = Boc, **9c**			
6	R^1 = COMe	4-Cl	93	**10f/11f/12f** = 92:2:6
	R^2 = Boc, **9c**			
7	R^1 = H	4-OMe	77	**10g/11g/12g** = 89:2:9
	R^2 = Boc, **9d**			
8	(−$CO_2CH_2CH_2$−), **9e**	4-OMe	88	**10h/11h/12h** = 91:5:4
9	R^1 = R^2 = Me, **9f**	4-OMe	-	-

[a] The reaction was carried out under air, by using the appropriate allylic amine **9a−f** (0.3 mmol), the appropriate arenediazonium tetrafluoroborate (0.25 mmol), $Pd_2(dba)_3$·dba (4 mol %, 10 mg), sodium acetate (3 equiv, 0.75 mmol, 0.061 g), and benzonitrile (1 mL). The reaction was stirred at room temperature with the reaction progress monitored by the evolution of N_2. Yields refer to mixtures of the three isomers (a single spot on TLC).

Table 3. Heck Arylation of Monosubstituted Allylamides 13a−f



entry	R^1	Ar	yield (%)[a]
1	R^1 = 4-FC_6H_4CO, **13a**	4-$MeOC_6H_4$	**14a**, 95
2	R^1 = C_6H_4CO, **13b**	4-$MeOC_6H_4$	**14b**, 60
3	R^1 = *p*-Ts, **13c**	4-$MeOC_6H_4$	**14c**, 98
4	R^1 = 4-FC_6H_4CO, **13a**	2-naphthyl	**14d**, 84
5	R^1 = *p*-Ts, **13c**	2-naphthyl	**14e**, 63
6	R^1 = 4-FC_6H_4CO, **13a**	4-FC_6H_4	**14f**, 79
7[b]	R^1 = 4-FC_6H_4CO, **13a**	3-BrC_6H_4	**14g**, 74
8	R^1 = *p*-Ts, **13c**	4-FC_6H_4	**14h**, 69
9	R^1= 4-FC_6H_4CO, **13a**	C_6H_5	**14i**, 72
10	R^1 = *p*-Ts, **13c**	C_6H_5	**14j**, 72
11	R^1 = CHO, **13d**	4-$MeOC_6H_4$	**14k**, 72
12	R^1 = CHO, **13d**	C_6H_5	**14l**, 52
13[c]	R^1 = Ac, **13e**	4-$MeOC_6H_4$	**14m**, 99
14[d]	R^1 = CF_3CO, **13f**	4-$MeOC_6H_4$	**14n**, 91

[a] The reaction was carried out under air, by using the appropriate allylic amine **13a−f** (0.3 mmol), the appropriate arenediazonium tetrafluoroborate (0.25 mmol), $Pd_2(dba)_3$·dba (4 mol %, 10 mg), sodium acetate (3 equiv, 0.75 mmol, 0.061 g), and benzonitrile (1 mL). The reaction was stirred at room temperature with the reaction progress monitored by the evolution of N_2. [b] The reaction was warmed at 60 °C, and 8 mol % of $Pd_2(dba)_3$ was used. [c] Ratio trans: *δ-trans*:*δ-cis*:*β*-substituted (single spot on TLC): 91:8:1. [d] Ratio trans: *δ-trans*:*δ-cis*:*β*-substituted (single spot on TLC): 87:4:9.

chelation of the ionic Ar−Pd species by the olefin and the carbonyl moieties with displacement of any other ligands present on the cationic palladium—the benzonitrile solvent, for example. This kind of arrangement provides the adequate regio- and sterocontrol by the substrate in the next step, migratory insertion, and all the subsequent steps in the catalytic cycle. The insertion of the aryl group at the γ-position would then be driven by stereoelectronic reasons, generating the six-membered chelated struture **C**. For the β-elimination step, the aryl group rotates to a more stable conformation (dba or other ligand is probably bound to Pd at this stage), thus allowing agostic interaction of Pd and one of the hydrogens of the CH_2 group (conformer **E**). This conformer then leads to the observed *trans* olefin. We believe that these types of Heck−Matsuda arylations constitute a good example of a substrate-directable reaction,[10] and contrary to current perception, steric effects seem to play a minor role in the regio- and stereocontrol of these Heck reactions.

Heck arylation of the homoallylic amide **15** was performed to probe the regio- and stereochemical outcome for a homoallylic

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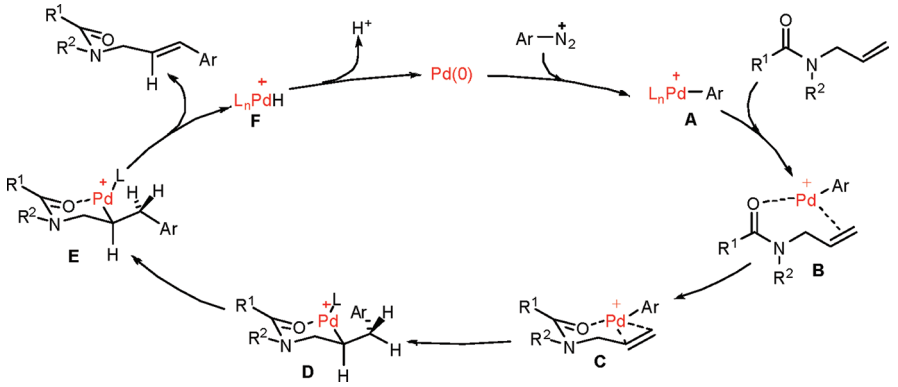
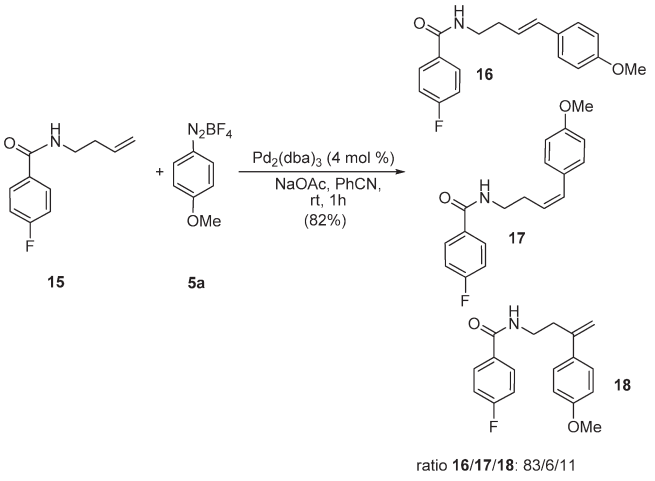
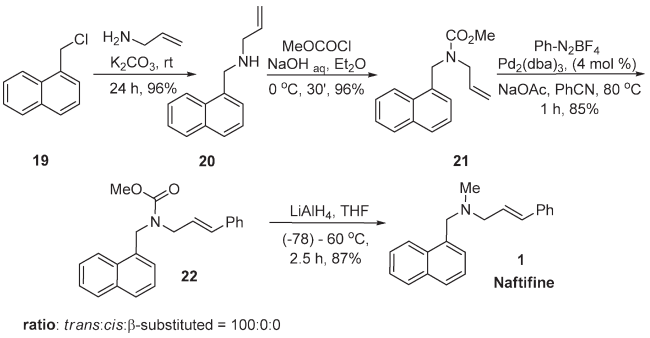
Scheme 3. Proposed Mechanism



Scheme 4. Heck−Matsuda Arylation of Homoallylic Benzamide 15



Scheme 5. Synthesis of Naftifine 1



system carrying less assistance of the coordinating groups, which would also validate to a greater extent the anchimeric mechanism proposed above. As expected on the basis of the proposed mechanism (see Scheme 4), a longer tether between the carbonyl group and the olefin resulted in lower stereoselectivity and mainly in a much lower regioselectivity (ratio **16**/**17**/**18** = 83:6:11), as illustrated in Scheme 4.

Having established the methodological background, we next turned our attention to the synthetic applications of this efficient Heck−Matsuda protocol. Our first target was the arylated allylamine derivative naftifine, which is a commercial drug possessing high antifungal activity. Naftifine acts at an earlier stage in the ergosterol pathway, inhibiting squalene epoxidase.[11] It is active against a wide range of pathogenic fungi both in vivo and in vitro.[12]

Thus, 1-(chloromethyl)naphthalene **19** was treated with K_2CO_3 and allylamine, providing the disubstituted allylamine **20** (96% yield), which was then converted into the methyl carbamate **21** with methyl chloroformate and NaOH (96% yield) (Scheme 5). Heck arylation of **21** with benzenediazonium tetrafluoroborate furnished the Heck adduct **22** in 85% yield with total regio- and stereochemical control in favor of the *E* isomer. Finally, reduction of the carbomethoxy group with $LiAlH_4$ proceeded in 87% yield (Scheme 5). Naftifine **1** was thus obtained in only four steps with an overall yield of 68%.

To extend the scope of the method further, we also accomplished concise total syntheses of two abamines. Abamines are a new series of abscisic acid (ABA) biosynthesis inhibitors which target the enzyme 9-*cis*-epoxycarotenoid dioxygenase (NCED), without causing lethal damage.[13] Thus, the abamines could be used to examine a broad range of physiological aspects involved in the function of ABA in plants.[14]

First, we generated the acyl chloride from the treatment of *p*-fluorobenzoic acid **23** with thionyl chloride (Scheme 6). Further reaction with allylamine delivered benzamide **13a** in 85% yield over the two steps. The key Heck arylation was performed between the benzamide and 3,4-dimethoxybenzenediazonium tetrafluoroborate under the optimized conditions established earlier. The desired product was obtained in 84% yield, with total regio- and stereochemical control in favor of the *E* isomer. Next, the reduction of the amide group was accomplished by AlH_3 (88% yield). To obtain abamine **2**, the alkylation of amine **25** was performed with methyl 2-chloroacetate in 85% yield. The abamine **2** was then obtained in five steps with an overall yield of 53%. Finally, aiming at synthesizing abamine SG **3**, we carried out the reductive amination reaction of secondary amine **25** with methyl 4-oxobutanoate (Scheme 6). After 72 h of stirring, abamine SG was formed in 88% yield (55% overall yield).

CONCLUSION

In summary, we describe herein an efficient, mild, and operationally simple Heck arylation of allylamine derivatives

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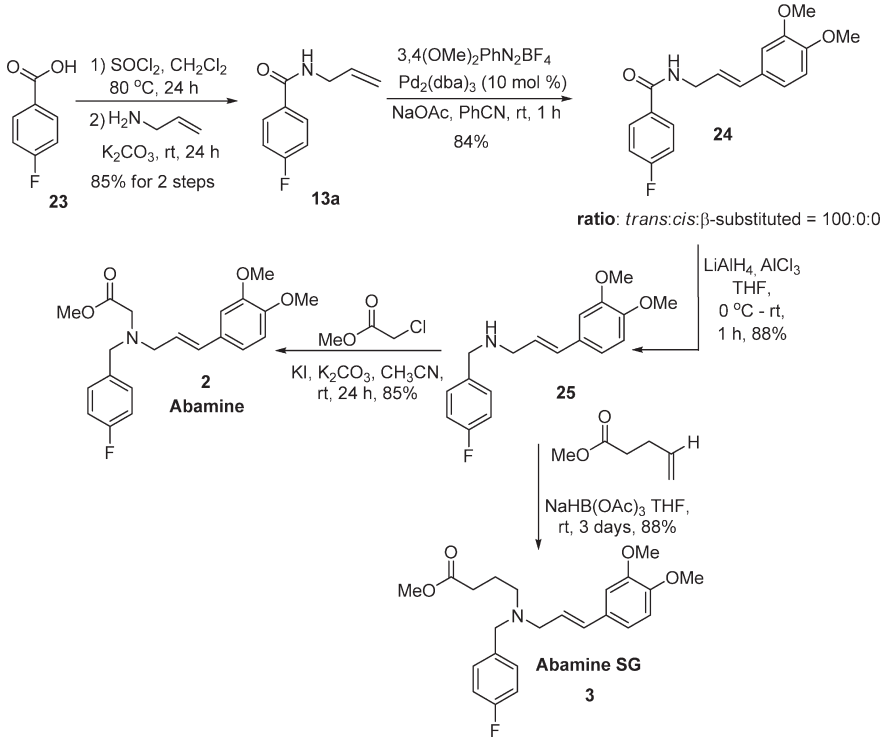
Scheme 6. Synthesis of Abamines 2 and 3



employing arenediazonium salts. The Heck−Matsuda reaction proceeds with remarkable regio- and stereochemical control, affording the corresponding arylated allylamine derivatives in good to high yields. The high regio- and stereocontrol observed with monosubstituted allylamides and allysulfonamides probably constitute the first examples of substrate-directable Heck−Matsuda reactions. Furthermore, using this method we synthesized the biologically active compounds naftifine **1**, abamine **2**, and abamine SG **3** by concise routes in high overall yields with regio- and stereochemical control in the key Heck arylation steps.

EXPERIMENTAL SECTION

Hydrogen nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 250, 300, and 500 MHz. Spectra were recorded in $CDCl_3$, DMSO-d_6, and MeOD solutions. Chemical shifts are reported in parts per million and referenced to the solvent peak of residual $CHCl_3$ or tetramethylsilane (TMS) as reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz, and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained at 62.5, 75, and 125 MHz. Spectra were recorded in $CDCl_3$ and DMSO-d_6 solutions. Chemical shifts are reported in parts per million and referenced to the solvent peak $CDCl_3$ or DMSO-d_6. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), ddd (double double doublet), tdd (triple double doublet), and m (multiplet). Microwave reactions were conducted in a commercial microwave synthesizer. The equipment consists of a continuous focused microwave-power delivery system with operator-selectable power output from 0 to 300 W. Reactions were performed in glass vessels (capacity 10 mL) sealed with a septum. Temperature measurements were conducted using an infrared temperature sensor mounted in the reaction vessel. All experiments were performed using a stirring option where the contents of the vessel were stirred by means of a rotating magnetic plate located below the floor of the microwave cavity together with a Teflon-coated magnetic stir bar in the vessel. All experiments were carried out with simultaneous cooling by passing compressed air through the microwave cavity while heating. Column chromatography was performed using silica gel (230−400 mesh) following the methods described by Still.[15] Thin layer chromatography (TLC) was performed using silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or stained with phosphomolibdic acid, followed by heating. Air- and moisture-sensitive reactions were conducted in flame-dried or oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry argon or N_2. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by using a mineral oil bath heated on a hot plate. All reagents purchased from a commercial supplier were used as received, except in the cases where the reagents were freshly distilled, which are detailed in the Experimental Section.

Some of the compounds produced by the Heck−Matsuda reaction of the allylic systems are mixtures of structural isomers which appear as a single spot on TLC and were extremely difficult to separate by flash chromatography. Therefore, these products were analyzed as mixtures, and the ratios between them were based on the characteristic peaks belonging to each specific isomer in the ^{1}H NMR spectra. The reader should make reference to the pure isomers **6e**, **7e**, and **8e** isolated by preparative HPLC, which were fully characterized concerning key structural assignments. Their spectra appear in the Supporting Information. When applicable, reference is also made to the presence of rotamers, which is a common phenomenon when dealing with amides and formamides in general.

Procedure for the Synthesis and Heck Arylations of Allyl Phthalimide 4. *2-Allylisoindoline-1,3-dione,* ***4***.[16] To a microwave test tube were added phthalic anhydride (0.74 g, 5 mmol), allylamine (0.31 g, 5.5 mmol), and acetic acid (2 mL). The reaction was stirred in a microwave reactor, at 150 °C (300 W power) for 2 h. After that time, the

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crude reaction mixture was diluted with EtOAc (50 mL) and washed with saturated $NaHCO_3$ (50 mL) and H_2O (2 × 20 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure as a solid residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 7:1 as eluent, R_f = 0.35) to give compound **4** as a white solid. Yield: 0.85 g (91%). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.79−7.76 (m, 2H), 7.65−7.62 (m, 2H), 5.87−5.74 (m, 1H), 5.20−5.09 (m, 2H), 4.22 (dt, J = 5.6 Hz, J = 1.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 75 MHz. δ (ppm): 167.8, 133.9, 132.0, 131.4, 123.2, 117.6, 39.9.

General Procedure for the Heck Arylation of Allylamine Derivatives. To a round-bottomed flask (or a test tube), under air, were added $Pd_2(dba)_3 \cdot dba$ (4 mol %, 10 mg), sodium acetate (3 equiv, 0.75 mmol, 0.061 g) and benzonitrile (1 mL). To the resulting suspension was added the appropriate allylamine derivative (1.2 equiv, 0.3 mmol) followed by the arenediazonium tetrafluoroborate (0.25 mmol). The reaction was stirred at room temperature and the reaction progress monitored by the evolution of N_2. After the nitrogen bubbling had stopped, the crude reaction mixture was filtered through a plug of silica and concentrated under reduced pressure. The product was then purified by flash chromatography (hexanes/ethyl acetate as eluent) to provide the corresponding aryl allylamine derivatives (single spot on TLC).

(E)-2-(3-(4-Methoxyphenyl)allyl)isoindoline-1,3-dione, ***6a***.[17] Yield: 0.072 g (99%). Ratio **6a**/**7a**/**8a** = 89:4:7 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.87−7.84 (m, 2H), 7.72−7.69 (m, 2H), 7.30 (d, J = 8.8 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 16.0 Hz, 1H), 6.17 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.43 (dd, J = 6.5, J = 1.0 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 168.0, 159.4, 133.9, 133.3, 132.1, 129.0, 127.7, 123.2, 120.4, 113.9, 55.2, 39.7. MS (EI): 294 (M+1), 293 (M), 146. HRMS calc for $C_{18}H_{15}NO_3$: 293.1047. Found: 293.1052. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.45), mp 137−140 °C.

(E)-2-(3-(2-Methoxyphenyl)allyl)isoindoline-1,3-dione, ***6b***. Yield: 0.068 g (93%). Ratio **6b**/**7b**/**8b** = 92:3:5 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.87−7.84 (m, 2H), 7.72−7.69 (m, 2H), 7.37 (d, J = 8.0 Hz, 1H), 7.21 (td, J = 8.0 Hz, J = 1.0 Hz, 1H), 6.99 (d, J = 16.0 Hz, 1H), 6.90−6.82 (m, 2H), 6.28 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.45 (d, J = 6.5 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 156.8, 133.8, 132.2, 128.9, 128.9, 127.1, 125.2, 132.3, 132.2, 120.5, 110.8, 55.4, 40.2. IR (film, cm^{-1}): 2936, 1713, 1579, 1243. MS (EI): 294 (M+1), 293 (M), 146. HRMS calcd for $C_{18}H_{15}NO_3$: 293.1052. Found: 293.1057. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.46), mp 98−101 °C.

(E)-2-(3-(4-Chlorophenyl)allyl)isoindoline-1,3-dione, ***6c***.[18] Yield: 0.070 g (95%). Ratio **6c**/**7c**/**8c** = 89:7:4 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.74−7.71 (m, 2H), 7.26 (s, 4H), 6.63 (d, J = 16.0 Hz, 1H), 6.28 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.45 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 134.7, 134.0, 133.5, 132.4, 132.1, 128.6, 127.7, 123.4, 123.3, 39.5. MS (EI): 298 (M+1), 297 (M), 262, 148. HRMS calcd for $C_{17}H_{12}ClNO_2$: 297.0557. Found: 297.0560. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.43), mp 171.5−172.5 °C.

(E)-2-(3-(3,4-Dichlorophenyl)allyl)isoindoline-1,3-dione, ***6d***.[17] Yield: 0.068 g (82%). Ratio **6d**/**7d**/**8d** = 93:5:2 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.74−7.71 (m, 2H), 7.42 (d, J = 2.0 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.18 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.45 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.8, 136.3, 133.0, 132.6, 132.0, 131.5, 131.2, 130.4, 128.2, 125.6, 124.9, 123.3, 39.3. MS (EI): 333 (M+2), 331 (M), 296, 183, 148. HRMS calcd for $C_{17}H_{11}Cl_2NO_2$: 331.0167. Found: 331.0189. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.36), mp 145−146 °C.

(E)-2-(3-(4-Fluorophenyl)allyl)isoindoline-1,3-dione, ***6e***.[18] Yield: 0.063 g (91%). Ratio **6e**/**7e**/**8e** = 95:2:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.74−7.71 (m, 2H), 7.34−7.29 (m, 2H), 7.00−6.94 (m, 2H), 6.64 (d, J = 16.0 Hz, 1H), 6.22 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.44 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz, δ (ppm): 167.9, 162.4 (d, J = 247.0 Hz, 1C), 134.0, 132.6, 132.4 (d, J = 3.0 Hz, 1C), 132.1, 128.1 (d, J = 8.0 Hz, 1C), 123.3, 122.4, 122.3, 115.6 (d, J = 21.0 Hz, 1C), 39.5. MS (EI): 282 (M+1), 281 (M), 263, 148. HRMS calcd for $C_{17}H_{12}FNO_2$: 281.0852. Found: 281.0850. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.51), mp 167−168 °C.

The synthesis of compound **6e** was also performed at the 5 mmol scale: a round-bottom flask was charged with 1.05 g of 4-fluorobenzenediazonium tetrafluoroborate (5 mmol), 1.121 g of allyl phthalimide **4** (6 mmol), 0.2 g of $Pd_2(dba)_3$ (0.2 mmol), and 18.45 g of NaOAc (15 mmol), dissolved in 5 mL of PhCN and stirred at room temperature for 1 h. After the nitrogen bubbling stopped, the crude reaction mixture was filtered through a plug of silica and concentrated under reduced pressure. The product was then purified by flash chromatography (hexanes/ethyl acetate as eluent) to provide 1.405 g of aryl allylamine derivative **6** in 91% as a mixture of isomers (ratio **6e**/**7e**/**8e** = 96:2:2), which appears as a single spot on TLC. The mixture of isomers was then recrystallyzed in $CHCl_3$ to provide the pure *trans* isomer **6e** in 83% yield.

(Z)-2-(3-(4-Fluorophenyl)allyl)-1H-indene-1,3(2H)-dione, ***7e***. ^{1}H NMR: $CDCl_3$, 500 MHz. δ (ppm): 7.88−7.86 (m, 2H), 7.75−7.74 (m, 2H), 7.40−7.38 (m, 2H), 7.14 (t, J = 8.5 Hz, 2H), 6.60 (d, J = 11.0 Hz, 1H), 5.68 (dt, J = 11.0 Hz, J = 6.5 Hz, 1H), 4.57 (dd, J = 6.5 Hz, J = 1.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 125 MHz. δ (ppm): 168.0, 161.9 (d, J = 247.0 Hz, 1C), 149.0, 147.0, 134.0, 132.2 (d, J = 3.0 Hz, 1C), 132.0, 130.9, 130.4 (d, J = 8.0 Hz, 1C), 125.7, 123.9, 115.3 (d, J = 21.0 Hz, 1C), 36.3. MS(EI): 282 (M+1), 281 (M), 148, 134. HRMS calcd for $C_{17}H_{12}FNO_2$: 281.0852. Found: 281.0844.

2-(2-(4-Fluorophenyl)allyl)-1H-indene-1,3(2H)-dione, ***8e***. ^{1}H NMR: $CDCl_3$, 500 MHz. δ (ppm): 7.87 (m, 2H), 7.75−7.73 (m, 2H), 7.50−7.47 (m, 2H), 7.04 (t, J = 8.5 Hz, 2H), 5.41 (s, 1H), 5.20 (t, J = 1.5 Hz, 1H), 4.70 (t, J = 1.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 125 MHz. δ (ppm): 167.9, 162.5 (d, J = 247.0 Hz, 1C), 141.5, 134.5 (d, J = 3.0 Hz, 1C), 134.0, 131.9, 128.1 (d, J = 8.0 Hz, 1C), 123.4, 115.3 (d, J = 21.0 Hz, 1C), 114.25, 114.24, 41.5. MS(EI): 282 (M+1), 281 (M), 263, 160. HRMS calcd for $C_{17}H_{12}FNO_2$: 281.0852. Found: 281.0856.

(E)-2-(3-(3-Fluorophenyl)allyl)isoindoline-1,3-dione, ***6f***. Yield: 0.069 g (99%). Ratio **6f**/**7f**/**8f** = 92:5:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.74−7.70 (m, 2H), 7.28−7.19 (m, 1H), 7.12−7.01 (m, 2H), 6.94 (td, J = 8.5 Hz, J = 2.5 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.46 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 164.9 (d, J = 247.0 Hz, 1C), 138.6 (d, J = 8.0 Hz, 1C), 134.0, 132.5 (d, J = 2.5 Hz, 1C), 132.0, 130.0 (d, J = 8.0 Hz, 1C), 124.2, 123.3, 122.4 (d, J = 2.5 Hz, 1C), 114.8 (d, J = 22.0 Hz, 1C), 113.1 (d, J = 22.0 Hz, 1C), 39.4. IR (film, cm^{-1}): 2921, 1708, 1578, 1428, 1394, 1105. MS (EI): 282 (M+1), 281 (M), 263, 148. HRMS calc for $C_{17}H_{12}FNO_2$: 281.0852. Found: 281.0848. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.49), mp 151−152 °C.

(E)-2-(3-(4-Bromophenyl)allyl)isoindoline-1,3-dione, ***6g***.[19] Yield: 0.083 g (98%). Ratio **6g**/**7g**/**8g** = 91:6:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.74−7.71 (m, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.44 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 135.1, 134.0, 132.5, 132.0, 131.6, 128.0, 123.5, 123.3, 121.7, 39.5. MS (EI): 342

(M+1), 341 (M), 193, 148, 115. HRMS calcd for $C_{17}H_{12}BrNO_2$: 341.0071. Found: 341.0051. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.55).

(E)-2-(3-(4-Iodophenyl)allyl)isoindoline-1,3-dione, ***6h***. Yield: 0.093 g (96%). Ratio **6h**/**7h**/**8h** = 86:9:5 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.87−7.83 (m, 2H), 7.75−7.70 (m, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.44 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ(ppm): 167.9, 137.5, 135.7, 134.0, 132.6, 132.1, 128.2, 123.7, 123.3, 93.2, 39.5. IR (film, cm^{-1}): 2916, 1702, 1468, 1397. MS (EI): 390 (M+2), 388 (M), 241, 148, 115. HRMS calcd for $C_{17}H_{12}INO_2$: 388.9913. Found: 388.9891. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.50), mp 186−188 °C.

2-Cinnamylisoindoline-1,3-dione, ***6i***.[20] Yield: 0.063 g (97%). Ratio **6i**/**7i**/**8i** = 93:4:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.85 (m, 2H), 7.73−7.70 (m, 2H), 7.34−7.21 (m, 5H), 6.69 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.46 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 136.2, 133.9, 133.7, 132.1, 128.5, 127.8, 126.5, 123.3, 122.6, 39.6. MS (EI): 264 (M+1), 263 (M), 245, 148, 115. HRMS calc for $C_{17}H_{13}NO_2$: 263.0946. Found: 263.0963. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.50), mp 153−155 °C.

(E)-2-(3-(Naphthalen-2-yl)allyl)isoindoline-1,3-dione, ***6j***.[21] Yield: 0.076 g (98%). Ratio **6j**/**7j**/**8j** = 98:0:2 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.98−7.85 (m, 2H), 7.79−7.71 (m, 6H), 7.57 (dd, J = 8.50 Hz, J = 2.0 Hz, 1H), 7.45−7.41 (m, 2H), 6.85 (d, J = 16.0 Hz, 1H), 6.44 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.52 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 168.2, 134.2, 134.1, 133.9, 133.7, 133.3, 132.4, 128.4, 128.2, 127.8, 126.9, 126.4, 126.2, 123.7, 123.5, 123.3, 39.9. MS (EI): 314 (M+1), 313 (M), 218, 166. HRMS calcd for $C_{21}H_{15}NO_2$: 313.1103. Found: 313.1131. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.54), mp 170−171 °C.

(E)-2-(3-(Biphenyl-4-yl)allyl)isoindoline-1,3-dione, ***6k***. Yield: 0.082 g (97%). Ratio **6k**/**7k**/**8k** = 92:4:4 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.89−7.85 (m, 2H), 7.74−7.70 (m, 2H), 7.59−7.51 (m, 4H), 7.45−7.32 (m, 5H), 6.73 (d, J = 16.0 Hz, 1H), 6.36 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.48 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 140.5, 140.6, 135.2, 133.9, 133.3, 132.1, 128.7, 127.3, 127.1, 126.9, 126.8, 123.3, 122.7, 29.6. IR (film, cm^{-1}): 2917, 1702, 1425, 1395, 955. MS (EI): 340 (M+1), 339 (M), 192, 165, 148. HRMS calcd for $C_{23}H_{17}NO_2$: 339.1259. Found: 339.1266. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.48), mp 195−196 °C.

(E)-2-(3-(4-Nitrophenyl)allyl)isoindoline-1,3-dione, ***6l***.[21] Yield: 0.066 g (86%). Ratio **6l**/**7l**/**8l** = 92:6:2 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 8.15 (d, J = 8.5 Hz, 2H), 7.89−7.85 (m, 2H), 7.75−7.72 (m, 2H), 7.49 (d, J = 8.5 Hz, 2H), 6.71 (d, J = 16.0 Hz, 1H), 6.48 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.50 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.8, 147.1, 142.6, 134.1, 131.9, 131.3, 127.7, 127.0, 123.9, 123.4, 39.3. MS (EI): 308 (M), 292, 291, 261, 161, 115. HRMS calcd for $C_{17}H_{12}N_2O_4$: 308.0797. Found: 308.0792. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.41).

(E)-2-(3-(Benzo[d][1,3]dioxol-5-yl)allyl)isoindoline-1,3-dione, ***6m***.[20] Yield: 0.064 g (84%). Ratio **6m**/**7m**/**8m** = 86:7:7 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.87−7.84 (m, 2H), 7.73−7.69 (m, 2H), 6.88 (d, J = 1.0 Hz, 1H), 6.80−6.69 (m, 2H), 6.13 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 5.92 (s, 2H), 4.42 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 147.9, 147.4, 133.9, 133.4, 132.1, 130.6, 123.2, 121.3, 120.9, 108.2, 105.7, 101.7, 39.6. MS (EI): 308 (M+1), 307 (M), 289, 160, 130. HRMS calc for $C_{18}H_{13}NO_4$: 307.0845. Found: 307.0897. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.49).

(E)-2-(3-p-Tolylallyl)isoindoline-1,3-dione, ***6n***.[22] Yield: 0.065 g (95%). Ratio **6n**/**7n**/**8n** = 91:4:5 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.88−7.84 (m, 2H), 7.73−7.69 (m, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 16.0 Hz, 1H), 6.26 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.44 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.9, 137.7, 133.9, 133.7, 133.4, 132.1, 129.2, 126.4, 123.2, 121.6, 39.7, 21.1. MS (EI): 277 (M), 259, 148, 130, 115. HRMS calcd for $C_{18}H_{15}NO_2$: 277.1103. Found: 277.1103. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.53), mp 165−166 °C.

Procedure for the Synthesis and the Heck Arylations of Allylamines 9a−f. *tert-Butyl Methyl Allyliminodicarbonate,* ***9a***.[23] Amine **9d** (0.84 g, 6 mmol) and THF (5.3 mL) were placed in a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was cooled to −78 °C, and *n*-BuLi (4.15 mL, 6.6 mmol, sol. 1.6 M) was added dropwise. The mixture was then allowed to warm to 0 °C and stirred for 15 min. The mixture was cooled again to −78 °C, and $ClCO_2Me$ (0.62 mL, 6.6 mmol) diluted in THF (8 mL) was added dropwise. The temperature was allowed to warm to room temperature and stirred for 1 h. Upon reaction completion (TLC), the mixture was diluted with EtOAc (20 mL) and washed with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 7:1 as eluent, R_f = 0.30) to give compound **9a** as a colorless oil. Yield: 0.91 g (71%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.92−5.76 (m, 1H), 5.21−5.11 (m, 2H), 4.25 (dt, J = 5.5 Hz, J = 1.5 Hz, 2H), 3.82 (s, 3H), 1.50 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 154.4, 151.5, 133.2, 116.4, 82.6, 53.5, 48.4, 27.8.

Di-tert-butyl Allyliminodicarbonate, ***9b***.[24] Amine **9d** (0.84 g, 6 mmol) and THF (5.3 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was cooled to −78 °C, and *n*-BuLi (4.15 mL, 6.6 mmol, sol. 1.6 M) was added dropwise. The mixture was then allowed to warm to 0 °C and stirred for 15 min. The mixture was cooled again to −78 °C, and $(Boc)_2O$ (1.44 g, 6.6 mmol) diluted in THF (8 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. Upon reaction completion (TLC), the mixture was diluted with EtOAc (20 mL) and washed with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 8:1 as eluent, R_f = 0.30) to give compound **9b** as a colorless oil. Yield: 1.05 g (62%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.90−5.76 (m, 1H), 5.20−5.11 (m, 2H), 4.18 (dt, J = 5.5 Hz, J = 1.0 Hz, 2H), 1.49 (s, 18H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 152.2, 133.7, 116.1, 82.2, 48.1, 28.0.

tert-Butyl Acetyl(allyl)carbamate, ***9c***. Amine **9d** (1.47 g, 10 mmol) and THF (10 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under a nitrogen atmosphere. The mixture was cooled to −78 °C, and *n*-BuLi (6.9 mL, 11 mmol, sol. 1.6 M) was added dropwise. The mixture was then allowed to warm to 0 °C and stirred for 15 min. The mixture was cooled again to −78 °C, and Ac_2O freshly distilled (1.03 mL, 11 mmol) diluted in THF (8 mL) was added dropwise. The temperature was allowed to warm to room temperature and stirred for 1 h. Upon reaction completion (TLC),

the mixture was diluted with EtOAc (20 mL) and washed with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 7:1 as eluent, R_f = 0.35) to give compound **9c** as a colorless oil. Yield: 1.75 g (71%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.85−5.69 (m, 1H), 5.14 (dq, J = 8.0 Hz, J = 1.5 Hz, 1H), 5.06 (t, J = 1.5 Hz, 1H), 4.27 (dt, J = 5.5 Hz, J = 1.5 Hz, 2H), 2.46 (s, 3H), 1.48 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 172.6, 152.9, 133.3, 116.3, 82.9, 46.1, 27.8, 26.6. HRMS calcd for $C_6H_9NO_3$ (M+H − C_4H_9): 143.0582. Found: 143.0592.

tert-Butyl Allylcarbamate, ***9d***.[25] Allylamine (0.75 mL, 10 mmol), $(Boc)_2O$ (2.39 g, 11 mmol), and ethanol were placed in a round-bottom flask equipped with a magnetic stir bar. Once bubbling of CO_2 had ceased, imidazole (0.81 g, 12 mmol) was added to the reaction mixture. The reaction was stirred at room temperature for 1 h, after which the mixture was diluted with EtOAc (20 mL) and washed with saturated $NaHCO_3$ (3 × 20 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 7:1 as eluent, R_f = 0.35) to give compound **9d** as a white solid. Yield: 1.33 g (85%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.91−5.88 (m, 1H), 5.20−5.08 (m, 2H), 4.60 (s, 1H), 3.74 (t, J = 6.5 Hz, 2H), 1.44 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 155.7, 134.8, 115.5, 79.2, 42.9, 28.2.

3-Allyloxazolidin-2-one, ***9e***.[26] NaH (5.2 mmol, 0.192 g) and THF (15 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was cooled to 0 °C, and oxazolidine (5 mmol, 0.435 g) was added dropwise. The mixture was stirred for an additional 1 h at 0 °C. Next, allyl bromide (7 mmol, 0.84 g) was added dropwise and the mixture refluxed overnight. Upon reaction completion, the mixture was diluted with EtOAc (30 mL) and washed with H_2O (2 × 20 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 8:1 as eluent, R_f = 0.45) to give compound **9e** as a colorless oil. Yield: 0.539 g (85%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.85−5.70 (m, 1H), 5.28−5.21 (m, 2H), 4.36 (dd, J = 9.0 Hz, J = 8.0 Hz, 2H), 3.88 (dt, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.55 (dd, J = 9.0 Hz, J = 8.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 157.8, 131.4, 117.8, 61.3, 46.2, 43.6.

(E)-tert-Butyl Methyl [3-(4-Methoxyphenyl)prop-2-en-1-yl]imidodicarbonate, ***10a***. Yield: 0.074 g (93%). Ratio **10a**/**11a**/**12a** = 91:5:4 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.30 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 16.0 Hz, 1H), 6.12 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.31 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 1.50 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 159.2, 154.5, 151.7, 132.1, 129.3, 127.5, 122.2, 113.9, 82.8, 55.2, 53.6, 48.3, 27.9. IR (film, cm^{-1}): 2978, 1791, 1750, 1689, 1512, 1368, 1249, 1154, 1035. MS(CI): 322 (M+H), 222, 147. HRMS calcd for $C_{17}H_{24}NO_5$ (M+H): 322.1649. Found: 322.1647. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.46).

(E)-tert-Butyl Methyl[3-(4-Chlorophenyl)prop-2-en-1-yl]imidodicarbonate, ***10b***. Yield: 0.074 g (92%). Ratio **10b**/**11b**/**12b** = 93:4:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.26 (s, 4H), 6.51 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.39 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.83 (s, 3H), 1.50 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 154.5, 151.6, 135.0, 133.3, 131.3, 128.7, 127.5, 125.2, 83.0, 53.8, 48.1, 28.0. IR (film, cm^{-1}): 2914, 1789, 1721, 1367, 1219, 1152, 843. MS(CI): 326 (M+H), 272, 270, 226, 153. HRMS calcd for $C_{16}H_{21}ClNO_4$ (M+H): 326.1154. Found: 326.1172. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.48).

(E)-tert-Butyl Methyl[3-(3-Bromophenyl)prop-2-en-1-yl]imidodicarbonate, ***10c***. Yield: 0.048 g (91%). Ratio **10c**/**11c**/**12c** = 93:4:3 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.42 (t, J = 1.7 Hz, 1H), 7.29−7.26 (m, 1H), 7.20−7.17 (m, 1H), 7.11−7.06 (m, 1H), 6.38 (d, J = 16.0 Hz, 1H), 6.13 (d, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.31 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.76 (s, 3H), 1.44 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 154.4, 151.5, 138.6, 130.9, 130.4, 130.0, 129.1, 126.1, 124.9, 122.6, 83.0, 53.7, 48.0, 27.9. IR (film, cm^{-1}): 2979, 1750, 1722, 1698, 1444, 1368. MS(CI): 316 [(M+H − C_4H_8) + 2], 314 (M+H − C_4H_8), 194, 120. HRMS calcd for $C_{16}H_{20}BrNO_4$ (M+H − C_4H_8): 314.0022. Found: 314.0021. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.52).

(E)-Di-tert-butyl 3-(4-Methoxyphenyl)allyliminodicarbonate, ***10d***.[9] Yield: 0.075 g (83%). Ratio **10d**/**11d**/**12d** = 93:2:5 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.31 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.51 (d, J = 16.0 Hz, 1H), 6.13 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.30 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.79 (s, 3H), 1.50 (s, 18H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 159.0, 152.2, 131.8, 129.4, 127.4, 122.6, 113.6, 82.1, 55.1, 49.1, 27.9. MS(CI): 364 (M+H), 263 (M), 208, 147. HRMS calcd for $C_{20}H_{30}NO_5$ (M+H): 364.2118. Found: 364.2120. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.55).

(E)-tert-Butyl Acetyl(3-(4-methoxyphenyl)allyl)carbamate, ***10e***. Yield: 0.074 g (98%). Ratio **10e**/**11e**/**12e** = 92:3:5 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.30 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.09 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.41 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 2.49 (s, 3H), 1.52 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 172.8, 159.2, 153.0, 132.3, 129.4, 127.5, 122.4, 113.9, 83.0, 55.2, 46.0, 28.0, 26.8. IR (film, cm^{-1}): 2978, 2837, 1734, 1695, 1608, 1512, 1368, 1249. MS(CI): 306 (M+H), 207, 206, 147. HRMS calc for $C_{17}H_{24}NO_4$ (M+H): 306.1705. Found: 306.1707. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.44).

(E)-tert-Butyl Acetyl(3-(4-chlorophenyl)allyl)carbamate, ***10f***. Yield: 0.087 g (99%). Ratio **10f**/**11f**/**12f** = 92:2:6 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.19 (s, 4H), 6.39 (dt, J = 16.0 Hz, J = 1.0 Hz, 1H), 6.12 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.35 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 2.43 (s, 3H), 1.45 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 172.8, 152.9, 135.1, 133.2, 131.4, 128.6, 127.5, 125.4, 83.2, 45.8, 28.0, 26.8. IR (film, cm^{-1}): 2977, 1735, 1696, 1491, 1368, 1222, 1148, 976. MS(CI): 310 (M+H), 254, 210, 115. HRMS calcd for $C_{16}H_{21}ClNO_3$: 310.1210. Found: 310.1200. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.55).

(E)-tert-Butyl 3-(4-methoxyphenyl)allylcarbamate, ***10g***. Yield: 0.050 g (77%). Ratio **10g**/**11g**/**12g** = 89:2:9 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.30 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.47 (d, J = 16.0 Hz, 1H), 6.10 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.62 (s, NH), 3.90 (t, J = 6.5 Hz, 2H), 3.79 (s, 3H), 1.46 (s, 9H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 159.1, 155.7, 131.0, 129.4, 127.4, 124.0, 113.9, 55.2, 29.6, 28.3. IR (film, cm^{-1}): 3356, 2969, 1692, 1512, 1244, 1173, 1027. MS(CI): 264 (M+H), 208, 148, 147. HRMS calcd for $C_{15}H_{22}NO_3$ (M+H): 264.1594. Found: 264.1592. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.50), mp 69−71 °C.

(E)-3-(3-(4-Methoxyphenyl)allyl)oxazolidin-2-one, ***10h***. Yield: 0.050 g (88%). Ratio **10h**/**11h**/**12h** = 91:5:4 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.31 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.04 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.34 (dd, J = 8.0 Hz, J = 9.0 Hz, 2H), 4.00 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H), 3.79 (s, 3H), 3.56 (dd, J = 9.0 Hz, J = 8.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 159.4, 158.2, 133.5, 128.7, 127.6, 120.7, 133.9, 61.7, 55.2, 46.5, 44.0. IR (film, cm^{-1}): 3473, 2895, 1739, 1513,

1242, 1026, 838, 759. MS(CI): 234 (M+H), 148, 247. HRMS calcd for $C_{13}H_{16}NO_3$ (M+H): 234.1125. Found: 234.1130. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, $R_f = 0.60$).

Procedure for the Synthesis and the Heck Arylations of Allylamines 13a−f. *N-Allyl-4-fluorobenzamide,* ***13a***.[27] *p*-Fluoro benzoic acid (1.4 g, 10 mmol) and CH_2Cl_2 (30 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. Next, freshly distilled $SOCl_2$ (1.08 mL, 15 mmol) and DMF (2 drops) were added to the reaction, and it was stirred at 80 °C for 24 h. Upon reaction completion, the solvent was removed under reduced pressure. The resulting residue was diluted with CH_2Cl_2 (3 × 20 mL) and the solvent removed once again under reduced pressure to assist in the removal of excess $SOCl_2$. Next, CH_2Cl_2 (40 mL), allylamine (80 mmol, 6.4 mL), and K_2CO_3 (11 mmol, 1.65 g) were added, and the reaction mixture was stirred for 24 h at room temperature. The mixture was then diluted with EtOAc (30 mL) and washed with saturated $NaHCO_3$ (3 × 20 mL). The organic phase was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford a solid residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 3:1 as eluent, $R_f = 0.35$) to give compound **13a** as a white solid. Yield: 1.52 g (85%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.82−7.76 (m, 2H), 7.15 (t, J = 8.5 Hz, 2H), 6.10 (s, 1H), 6.02−5.86 (m, 1H), 5.31 (dq, J = 17.0 Hz, J = 3.0 Hz, J = 1.5 Hz, 1H), 5.23 (dq, J = 11.0 Hz, J = 3.0 Hz, J = 1.5 Hz, 1H), 4.08 (tt, J = 5.8 Hz, J = 1.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.4, 164.5 (d, J = 250.0 Hz, 1C), 133.9, 130.5 (d, J = 3.0 Hz, 1C), 129.3 (d, J = 8.0 Hz, 1C), 116.4, 115.3 (d, J = 21.0 Hz, 1C), 42.5. MS(CI): 179 (M), 164, 83, 48. HRMS calcd for $C_{10}H_{10}FNO$: 179.0746. Found: 179.0756. The product was obtained as a white solid. mp 65−67 °C.

N-Allyl-benzamide, ***13b***.[25] To a solution of benzoyl chloride (2.40 mL, 20.7 mmol) in CH_2Cl_2 (80 mL) was added dropwise a solution of allylamine (1.52 mL, 20.0 mmol) and Et_3N (2.90 mL, 20.7 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After the addition, the reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water (50 mL), and the aqueous layer was washed with CH_2Cl_2 (50 mL). The organic layers were combined and evaporated under vacuum. The residue was subjected to column chromatography on silica gel to afford a solid residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 2:1 as eluent, $R_f = 0.40$) to give compound **13b** as a white solid. Yield: 2.93 g (91%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.81 (d, J = 8.5 Hz, 2H), 7.48−7.32 (m, 3H), 7.08 (s, 1H), 5.96−5.80 (m, 1H), 5.25−5.08 (m, 2H), 4.01 (t, J = 5.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.4, 134.2, 134.0, 131.1, 128.2, 126.9, 116.0, 42.2.

N-Allyl-4-methylbenzenesulfonamide, ***13c***.[25] Allylamine (5 mmol, 0.285 g) and Et_3N (7.8 mmol, 1.1 mL) dissolved in CH_2Cl_2 (55 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. Next, tosyl chloride (7.8 mmol, 1.48 g) was added, and the reaction was stirred for 24 h at room temperature. After this time, saturated NH_4Cl (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford a solid residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, $R_f = 0.50$) to give compound **13c** as a white solid. Yield: 0.96 g (91%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.77 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.76−5.64 (m, 1H), 5.16−5.01 (m, 3H), 3.57 (tt, J = 7.5 Hz, J = 1.5 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 143.2, 136.7, 132.8, 129.5, 126.9, 117.3, 45.5, 21.3.

N-Allylformamide, ***13d***.[28] Ethyl formate (14.16 g, 200 mmol) was placed in a flame-dried round-bottom flask equipped with a magnetic stir bar under a nitrogen atmosphere and cooled to 0 °C. Next, allylamine (5.71 mL, 100 mmol) was added dropwise, and the reaction was stirred overnight at room temperature. The solvent was then removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, $R_f = 0.45$) to give compound **13d** as a colorless oil. Yield: 6.80 g (80%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 8.15 (s, 1H), 7.78 (s, 1H), 5.89−5.74 (m, 1H), 5.22−5.09 (m, 2H), 3.84 (t, J = 5.5 Hz, 2H). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 161.1, 132.9, 115.2, 39.5.

N-Allylacetamide, ***13e***.[26] The procedure for the preparation of this allylamine is the same as described for allylamine **13c** but using freshly distilled acetic anhydride instead of tosyl chloride. The product was isolated as an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 6:1 as eluent, $R_f = 0.40$) to give compound **13e** as a colorless oil. Yield: 1.48 g (91%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 5.90−5.75 (m, 2H), 5.21−5.06 (m, 2H), 4.34−4.31 (m, 2H), 2.41 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 169.9, 134.1, 116.2, 41.9, 23.0.

N-Allyl-2,2,2-trifluoroacetamide, ***13f***.[29] Allylamine (0.94 g, 16.5 mmol) was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 °C. Pyridine (3.32 mL, 41.26 mmol) was added to the stirring solution of the amine, followed by dropwise addition of freshly distilled trifluoroacetic anhydride (2.91 mL, 20.64 mmol) over 30 min. The reaction was allowed to warm to room temperature and stirred for 3 h. The reaction mixture was poured into 0.5 M HCl (30 mL) and vigorously stirred for 5 min. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with HCl 0.5 N (20 mL), H_2O (20 mL), and saturated $NaHCO_3$ and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford an oil residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 6:1 as eluent, $R_f = 0.35$) to give compound **13f** as a colorless oil. Yield: 3.41 g (80%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 6.38 (s, 1H), 5.90−5.78 (m, 1H), 5.30−5.23 (m, 2H), 3.99 (t, J = 5.8 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 157.3 (q, J = 37.0 Hz, 1C), 131.7, 117.7, 115.8 (q, J = 287.0 Hz, 1C), 42.0.

(E)-4-Fluoro-N-(3-(4-methoxyphenyl)allyl)benzamide, ***14a***. Yield: 0.067 g (95%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.87−7.82 (m, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.09 (t, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.61 (s, NH), 6.53 (d, J = 16.0 Hz, 1H), 6.13 (d, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.2 (td, J = 1.0 Hz, J = 6.5 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 164.6 (d, 251.0 Hz, 1C), 159.2, 132.0, 130.5 (d, J = 3.0 Hz, 1C), 129.2 (d, J = 8.0 Hz, 1C), 129.1, 125.5, 122.8, 115.5 (d, J = 21.0 Hz, 1C), 113.9, 55.1, 42.4. IR (film, cm^{-1}): 3315, 2912, 1673, 1502, 1256, 851. MS(CI): 285 (M), 164, 146, 123. HRMS calcd for $C_{17}H_{16}FNO_2$: 285.1165. Found: 285.1180. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, $R_f = 0.50$), mp 137−141 °C.

(E)-N-(3-(4-Methoxyphenyl)allyl)benzamide. ***14b***.[30] Yield: 0.040 g (60%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.81−7.77 (m, 2H), 7.49−7.38 (m, 3H), 7.28 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.39 (s, 1H), 6.13 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.20 (td, J = 1.0 Hz, J = 6.5 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 167.2, 159.3, 134.4, 132.0, 131.4, 129.2, 128.5, 127.5, 126.9, 123.0, 113.9, 55.2, 42.1. MS(EI): 161, 121, 105, 77. HRMS calcd for $C_{10}H_{11}NO$ (M − C_7H_8O): 161.0841. Found: 161.0854. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, $R_f = 0.65$), mp 121−122 °C.

(E)-N-(3-(4-Methoxyphenyl)allyl)-4-methylbenzenesulfonamide, ***14c***.[31] Yield: 0.077 g (98%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.77 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.38 (d, J = 16.0 Hz, 1H), 5.87 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.42 (t, J = 6.0 Hz, 1H), 3.79 (s, 3H), 3.73 (td, J = 6.5 Hz, J = 1.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 159.2, 143.3, 137.0, 132.4, 129.6, 128.8, 127.5, 127.1, 121.7, 113.8, 55.1, 45.4, 21.3. MS(EI): 317 (M), 160, 146, 91. HRMS calcd for $C_{17}H_{19}NO_3S$: 317.1086. Found: 317.1079. The product as obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.39), mp 107−108 °C.

(E)-4-Fluoro-N-(3-(naphthalen-2-yl)allyl)benzamide, ***14d***. Yield: 0.064 g (84%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.96−7.91 (m, 2H), 7.79−7.74 (m, 2H), 7.65−7.61 (m, 1H), 7.47−7.40 (m, 2H), 7.19 (t, J = 8.5 Hz, 2H), 6.76 (d, J = 16.0 Hz, 1H), 6.45 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.20 (dd, J = 6.5 Hz, J = 1.0 Hz, 2H). NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.2, 164.7 (d, J = 251.0 Hz, 1C), 133.8, 133.5, 133.0, 132.7, 130.5 (d, J = 3.0 Hz, 1C), 129.3 (d, J = 8.0 Hz, 1C), 128.2, 127.9, 127.6, 126.4, 126.3, 125.5, 123.4, 115.6 (d, J = 21.0 Hz, 1C), 42.2. IR (film, cm^{-1}): 3447, 2923, 1626, 1503, 1241, 1161. MS(EI): 306 (M+1), 286, 167, 123, 95. HRMS calcd for $C_{20}H_{17}FNO$: 306.1289. Found: 306.1294. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.55), mp 154−155 °C.

(E)-4-Methyl-N-(3-(naphthalen-2-yl)allyl)benzenesulfonamide, ***14e***. Yield: 0.053 g (63%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.80−7.68 (m, 5H), 7.55 (s, 1H), 7.44−7.36 (m, 3H), 7.24 (d, J = 8.5 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.08 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.93 (t, J = 6.0 Hz, 1H), 3.77 (t, J = 6.0 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 143.4, 137.0, 133.5, 133.3, 132.9, 129.6, 128.1, 127.9, 127.5, 127.1, 126.4, 126.2, 125.9, 124.4, 123.3, 45.4, 21.3. IR (film, cm^{-1}): 3228, 3055, 1438, 1322, 1158, 654. MS(EI): 339 (M+2), 338 (M+1), 337 (M). HRMS calcd for $C_{20}H_{19}NO_2S$: 337.1136. Found: 337.1159. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.45), mp 123−124 °C.

(E)-4-Fluoro-N-(3-(4-fluorophenyl)allyl)benzamide, ***14f***. Yield: 0.053 g (79%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.84−7.78 (m, 2H), 7.33−7.26 (m, 2H), 7.09 (t, J = 8.5 Hz, 2H), 6.98 (t, J = 8.5 Hz, 2H), 6.53 (d, J = 16.0 Hz, 1H), 6.40 (s, 1H), 6.17 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.20 (td, J = 6.5 Hz, J = 1.0 Hz, 2H). NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.2, 164.7 (d, J = 251.0 Hz, 1C), 162.4 (d, J = 251.0 Hz, 1C), 132.5 (d, J = 3.0 Hz, 1C), 131.4, 130.5 (d, J = 3.0 Hz, 1C), 129.2 (d, J = 8.0 Hz, 1C), 129.2 (d, J = 8.0 Hz, 1C), 125.0, 124.9, 115.6 (d, J = 21.0 Hz, 1C), 115.5 (d, J = 21.0 Hz, 1C), 42.1. IR (film, cm^{-1}): 3438, 3071, 2897, 1634, 1551, 1234, 1104. MS(EI): 273 (M), 164, 123, 95. HRMS calcd for $C_{16}H_{13}F_2NO$: 273.0965. Found: 273.0916. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.50), mp 133−134 °C.

(E)-N-(3-(3-Bromophenyl)allyl)-4-fluorobenzamide, ***14g***. Yield: 0.061 g (74%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.78−7.71 (m, 2H), 7.44 (t, J= 1.7 Hz, 1H), 7.31−7.27 (m, 1H), 7.11 (d, J = 8.5 Hz, 1H), 7.04 (t, J = 8.5 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 6.26−6.16 (m, 2H), 4.16 (td, J = 6.5 Hz, J = 1.3 Hz, 2H). NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.2, 164.7 (d, J = 251.0 Hz, 1C), 138.5, 130.9, 130.6, 130.4 (d, J = 3.0 Hz, 1C), 130.1, 129.2 (d, J = 8.0 Hz, 1C), 129.2, 126.9, 125.0, 122.7, 115.6 (d, J = 21.0 Hz, 1C), 41.9. IR (film, cm^{-1}): 3278, 2981, 1632, 1603, 1505, 1325, 1232, 966. MS(CI): 336 (M+H + 2), 334 (M+H), 224, 256, 194, 152. HRMS calcd for $C_{16}H_{14}BrFNO$ (M+H): 334.0243. Found: 334.0256. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.40).

(E)-N-(3-(4-Fluorophenyl)allyl)-4-methylbenzenesulfonamide, ***14h***.[32] Yield: 0.052 g (69%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.77 (d, J = 8.5 Hz, 2H), 7.29 (d, 8.5 Hz, 2H), 7.23−7.17 (m, 2H), 6.96 (t, J = 8.5 Hz, 2H), 6.4 (d, J = 16.0 Hz, 1H), 5.92 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.65 (t, J = 6.0 Hz, 1H), 3.73 (td, J = 6.5 Hz, J = 1.0 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 164.2 (d, J = 252.0 Hz, 1C), 143.5, 137.0, 132.2 (d, J = 3.0 Hz, 1C), 131.8, 129.7, 127.9 (d, J = 8.0 Hz, 1C), 127.1, 123.9, 123.0, 111.5 (d, J = 21.0 Hz, 1C), 43.4, 21.4. MS(EI): 306 (M+1), 305 (M), 212, 171. HRMS calcd for $C_{16}H_{16}FNO_2S$: 305.0886. Found: 305.0898. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.48).

N-Cinnamyl-4-fluorobenzamide, ***14i***.[33] Yield: 0.045 g (72%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.84−7.78 (m, 2H), 7.37−7.23 (m, 5H), 7.08 (t, J = 8.5 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.43 (s, 1H), 6.25 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.21 (t, J = 6.5 Hz, 2H). NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.2, 164.6 (d, J = 251.0 Hz, 1C), 136.3, 132.5, 130.3 (d, J = 3.0 Hz, 1C), 129.2 (d, J = 8.0 Hz, 1C), 128.5, 127.7, 126.3, 125.2, 115.5 (d, J = 21.0 Hz, 1C), 42.1. MS(EI): 255 (M), 218, 164, 123, 115. HRMS calcd for $C_{16}H_{14}FNO$: 255.1059. Found: 255.1054. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.55), mp 116−118 °C.

N-Cinnamyl-4-methylbenzenesulfonamide, ***14j***.[32] Yield: 0.051 g (72%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.77 (d, J = 8.5 Hz, 2H), 7.30−7.24 (m, 7H), 6.42 (d, J = 16.0 Hz, 1H), 6.0 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.69 (s, 1H), 3.74 (t, J = 6.5 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 143.5, 137.0, 136.0, 133.0, 129.7, 128.5, 127.9, 127.1, 126.3, 124.0, 45.4, 21.4. MS(EI): 289 (M+H+1), 288 (M+H). HRMS calcd for $C_{16}H_{18}NO_2S$ (M+H): 288.1053. Found: 288.1027. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.52), mp 107−108 °C.

(E)-N-(3-(4-Methoxyphenyl)allyl)formamide, ***14k***.[34] Yield: 0.034 g (72%). The *trans* isomer was obtained exclusively. The ^{1}H NMR and ^{13}C NMR spectra show the presence of two rotamers in 4.71:1 ratio. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 8.19 (s, 1H), 7.26 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H), 6.14−5.95 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 160.9, 159.3, 132.0, 129.0, 127.5, 122.4, 113.9, 55.2, 40.1. MS(EI): 192 (M+1), 191 (M), 146, 131, 103. HRMS calcd for $C_{11}H_{13}NO_2$: 191.0946. Found: 191.0946. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.35), mp 73−74 °C.

N-Cinnamylformamide, ***14l***.[35] Yield: 0.020 g (22%). The *trans* isomer was obtained exclusively. The ^{1}H NMR and ^{13}C NMR spectra show the presence of two rotamers in 4.96:1 ratio. ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 8.23 (s, 1H), 7.36−7.23 (m, 5H), 6.53 (d, J = 16.0 Hz, 1H), 6.18 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 5.81 (s, 1H), 4.08 (t, J = 6.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 160.9, 136.2, 132.5, 128.5, 127.8, 126.3, 124.7, 40.0. MS(EI): 162 (M+1), 161 (M), 116, 115. HRMS calcd for $C_{10}H_{11}NO$: 161.0841. Found: 161.0843. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.35).

(E)-N-(3-(4-Methoxyphenyl)allyl)acetamide, ***14m***.[36] Yield: 0.050 g (99%). Ratio *trans*:*cis*:β-substituted = 91:8:1 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.28 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.45 (d, J = 16.0 Hz, 1H), 6.04 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 5.73 (s, 1H), 3.99 (t. J = 6.5 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR: $CDCl_3$, 75 MHz. δ (ppm): 169.8, 159.3, 131.8, 129.2, 127.5, 123.1, 113.9, 55.2, 41.7, 23.3. MS(EI): 206 (M+1), 205 (M), 148, 147. HRMS calcd for $C_{12}H_{15}NO_2$: 205.1103. Found: 205.1122. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.49).

(E)-2,2,2-Trifluoro-N-(3-(4-methoxyphenyl)allyl)acetamide, ***14n***. Yield: 0.058 g (91%). Ratio *trans*:*cis*:β-substituted = 87:4:9 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.20 (d, J = 8.5 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 6.00 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.22 (dd, J = 6.5 Hz, J = 1.3 Hz), 3.71

(s, 3H). ^{13}C NMR: $CDCl_3$, 75 MHz. δ (ppm): 159.4, 157.3 (q, J = 37.0 Hz, 1C), 133.4, 128.6, 127.6, 120.3, 117.0 (q, J = 287.0 Hz, 1C), 113.9, 55.1, 41.9. IR (film, cm^{-1}): 3282, 2956, 1702, 1513, 1183, 1162, 1034, 829. MS(EI): 260 (M+1), 259 (M), 148, 147. HRMS calcd for $C_{12}H_{13}F_3NO_2$: 260.0898. Found: 260.0891. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.45), mp 91−92 °C.

N-(But-3-enyl)-4-fluorobenzamide, ***15***. 4-Fluorobenzoic acid (1.4 g, 10 mmol) and CH_2Cl_2 (30 mL) were placed in a flame-dried round-bottom flask equipped with a magnetic stir bar under a nitrogen atmosphere. Next, freshly distilled $SOCl_2$ (1.08 mL, 15 mmol) and DMF (2 drops) were added, and the reaction was stirred at 80 °C for 24 h. The solvent was then removed under reduced pressure, and the mixture was diluted with CH_2Cl_2 (3 × 20 mL). Once again, the solvent was removed under reduced pressure to assist in the removal of excess $SOCl_2$. THF (100 mL) was then added, and the mixture was cooled to 0 °C. Next, NH_4OH (300 mL, 30% solution) was added, and the mixture was stirred for 1 h. The mixture was then extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford a white solid corresponding to 4-fluorobenzamide, which was used without purification in the next step. The next step started with the addition of NaH (solution 60%, 10 mmol, 0.432 g) and DMF (10 mL) to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. Next, the system was cooled to 0 °C, and the 4-fluorobenzamide prepared above (10 mmol, 1.39 g) was added dropwise. The reaction was stirred for 30 min, and then 4-bromobut-1-ene (3 mmol, 0.3 mL) dissolved in DMF (3 mL) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 30 h. Next, saturated NH_4Cl (20 mL) was added, and the organic layer was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford a solid residue. The crude product was purified by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.53) to give compound **15** as a white solid. Mp 44−45 °C. Yield: 0.17 g (31%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 7.77−7.72 (m, 2H), 7.08 (t, J = 8.5 Hz, 2H), 6.19 (s, 1H), 5.89−5.73 (m, 1H), 5.18−5.09 (m, 2H), 3.51 (dt, J = 6.5 Hz, J = 5.7 Hz, 2H), 2.37 (qt, J = 6.5 Hz, J = 1.2 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.3, 164.5 (d, J = 251.0 Hz, 1C), 135.2, 130.8 (d, J = 3.0 Hz, 1C), 129.1 (d, J = 8.0 Hz, 1C), 117.4, 115.5 (d, J = 21.0 Hz, 1C), 38.8, 33.7. IR (film, cm^{-1}): 3279, 1634, 1558, 1507, 1330, 1238. MS(CI): 194 (M+H), 174, 152, 123. HRMS calcd for $C_{11}H_{13}FNO$ (M+H): 194.0976. Found: 194.0974.

(E)-4-Fluoro-N-(4-(4-methoxyphenyl)but-3-enyl)benzamide, ***16***. Yield: 0.061 g (82%). Ratio **16**/**17**/**18** = 83:6:11 (single spot on TLC). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.69−7.64 (m, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.00 (t, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 6.12 (s, 1H), 5.98 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 3.73 (s, 3H), 3.50 (q, J = 6.5 Hz, 2H), 2.43 (qd, J = 6.5 Hz, J = 1.1 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 166.4 (d, J = 251.0 Hz, 1C), 159.0, 132.0, 130.8 (d, J = 3.0 Hz, 1C), 129.8, 129.1 (d, J = 8.0 Hz, 1C), 127.2, 124.4, 115.5 (d, J = 21.0 Hz, 1C), 113.9, 55.2, 39.4, 33.0. IR (film, cm^{-1}): 3292, 2918, 1634, 1550, 1511, 1249. MS(EI): 301 (M+H+1), 300 (M+H), 192, 160. HRMS calcd for $C_{18}H_{19F}NO_2$ (M+H): 300.1394. Found: 300.1407. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.48), mp 139−140 °C.

N-(Naphthalen-1-ylmethyl)prop-2-en-1-amine, ***20***.[37] Allylamine (80 mmol, 6.4 mL), K_2CO_3 (12 mmol, 1.65 g), and 1-(chloromethyl)naphthalene **19** were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. The reaction mixture was stirred for 24 h. After this time, the mixture was diluted with EtOAc (40 mL) and washed with saturated $NaHCO_3$ (3 × 15 mL). The organic layer was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give an oil residue. Compound **20** was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.60). Yield: 1.91 g (96%). ^{1}H NMR: $CDCl_3$, 250 MHz. δ (ppm): 8.15−8.12 (m, 1H), 7.90−7.77 (m, 2H), 7.59−7.41 (m, 4H), 6.09−5.93 (m, 1H), 5.30−5.19 (m, 2H), 4.25 (s, 2H), 3.41 (dt, J = 6.0 Hz, J = 1.0 Hz, 2H). ^{13}C NMR: $CDCl_3$, 62.5 MHz. δ (ppm): 136.9, 135.9, 133.9, 131.8, 128.7, 127.7, 126.1, 126.1, 125.6, 125.4, 123.7, 116.2, 52.3, 50.84. MS(EI): 198 (M+1), 197 (M), 169, 142, 141. HRMS calcd for $C_{14}H_{15}N$: 197.1204. Found: 197.1205.

Methyl Allyl(naphthalen-1-ylmethyl)carbamate, ***21***. Methyl chloroformate (1.04 g, 11 mmol) was added dropwise under stirring to a cooled (0 °C) solution of amine **20** (1.97 g, 10 mmol) in Et_2O (50 mL) followed by addition of NaOH solution (440 mg, 11 mmol, in 5 mL of water). The mixture was stirred at 0 °C for 30 min, when the ethereal layer was separated, washed with aq. HCl (4 M, 3 × 30 mL), water (30 mL), and dried over Na_2SO_4. After evaporation of the solvent, the crude oily residue was purified by chromatography. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.55). Yield: 2.44 g (96%). ^{1}H NMR: DMSO-d_6, 250 MHz, 120 °C. δ (ppm): 8.09−8.05 (m, 1H), 7.93−7.81 (m, 2H), 7.55−7.34 (m, 4H), 5.81−5.66 (m, 1H), 5.09−5.00 (m, 2H), 4.92 (s, 2H), 3.82 (dt, J = 6.5 Hz, J = 1 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR: DMSO-d_6, 62.5 MHz, 120 °C. δ (ppm): 155.6, 133.0, 132.9, 132.3, 130.6, 127.7, 127.0, 125.4, 124.9, 124.7, 123.4, 122.3, 115.7, 51.6, 47.8, 46.7. IR (film, cm^{-1}): 2955, 1703, 1472, 1246, 1144, 771. MS(EI): 257 (M+2), 256 (M+1), 255 (M). HRMS calcd for $C_{16}H_{17}NO_2$: 255.1259. Found: 255.1262.

Methyl Cinnamyl(naphthalen-1-ylmethyl)carbamate, ***22***. Yield: 0.07 g (85%). The *trans* isomer was obtained exclusively. ^{1}H NMR: DMSO-d_6, 250 MHz, 120 °C. δ (ppm): 8.13−8.09 (m, 1H), 7.92−7.80 (m, 2H), 7.54−7.40 (m, 4H), 7.26−7.20 (m, 5H), 6.38 (d, J = 16.0 Hz, 1H), 6.09 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.99 (s, 2H), 3.99 (dd, J = 6.5 Hz, J = 1.5 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR: DMSO-d_6, 62.5 MHz, 120 °C. δ (ppm): 155.6, 136.0, 132.9, 132.4, 131.0, 130.6, 127.7, 127.5, 127.0, 126.5, 125.4, 124.9, 124.8, 124.7, 124.4, 122.3, 51.6, 47.3, 46.9. IR (film, cm^{-1}): 2924, 2853, 1700, 1469, 1245. MS(EI): 333 (M+2), 332 (M+1), 331 (M). HRMS calcd for $C_{22}H_{21}NO_2$: 331.1572. Found: 331.1568. The product was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent), R_f = 0.60.

(E)-N-Methyl-N-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine, ***1***.[38] Carbamate **22** (0.1 mmol, 0.036 g) and THF (2 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. Next, the reaction was cooled to −78 °C, and $LiAlH_4$ (0.2 mmol, 0.2 mL, solution 1 M in THF) was added dropwise. The reaction mixture was then heated at 60 °C under stirring for 2.5 h. Upon reaction completion, the mixture was diluted with EtOAc (10 mL) and washed with saturated $NaHCO_3$ (3 × 10 mL). The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Compound **1** was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 4:1 as eluent, R_f = 0.70). Yield: 0.025 g (87%). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 8.22 (d, J = 8.1 Hz, 1H), 7.78−7.88 (m, 2H), 7.47−7.17 (m, 9H), 6.50 (d, J = 16.0 Hz, 1H), 6.30 (dt, J = 16.0, J = 6.5 Hz, 1H), 3.87 (s, 2H), 3.20 (d, ^{1} = 6.5 Hz, 2H), 2.20 (s, 3H). ^{13}C NMR: $CDCl_3$, 75 MHz. δ (ppm): 137.0, 134.7, 133.8, 132.6, 132.4, 128.5, 128.4, 127.9, 127.5, 127.4, 127.3, 126.2, 125.8, 125.5, 125.0, 124.5, 60.3, 60.0, 42.4. MS(CI): 288 (M+1), 287 (M), 286, 196, 141, 115. HRMS calcd for $C_{21}H_{22}N$: 288.1752. Found: 288.1749.

(E)-N-(3-(3,4-Dimethoxyphenyl)allyl)-4-fluorobenzamide, ***24***. Yield: 0.066 g (84%). The *trans* isomer was obtained exclusively. ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.84−7.87 (m, 2H), 7.11 (t, J = 8.5 Hz, 2H), 6.89−6.77 (m, 3H), 6.50 (d, J = 16.0 Hz, 1H), 6.18 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 4.20 (t, J = 6.5 Hz, 2H), 3.85 (s, 6H). ^{13}C NMR: $CDCl_3$, 75 MHz.

δ (ppm): 166.2, 164.5 (d, J = 251.0 Hz, 1C), 148.9, 148.9, 132.3, 130.3 (d, J = 3.0 Hz, 1C), 129.4, 129.2 (d, J = 8.0 Hz, 1C), 123.1, 119.6, 115.5 (d, J = 21.0 Hz, 1C), 111.0, 108.6, 55.8, 55.7, 42.2. IR (film, cm^{-1}): 3297, 2999, 1635, 1571, 1271, 1162, 960, 792. MS(EI): 316 (M+1), 315 (M), 178.177. HRMS calcd for $C_{18}H_{18}FNO_3$: 315.1271. Found: 315.1280. The product was obtained as a white solid after purification by flash chromatography (hexanes/ethyl acetate 3:2 as eluent, R_f = 0.45), mp 130−132 °C.

(E)-3-(3,4-Dimethoxyphenyl)-N-(4-fluorobenzyl)prop-2-en-1-amine, ***25***. Dried aluminum trichloride (0.06 mmol, 0.008 g) and THF (1 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen atmosphere. The reaction mixture was cooled to 0 °C and stirred for 10 min. Next, a solution of $LiAlH_4$ (0.2 mmol, 0.2 mL, solution 2 M in THF) was added dropwise, and the reaction was stirred for 10 min, followed by dropwise addition of amide **24** (0.1 mmol, 0.031 g in 1 mL of THF). The temperature was then increased to room temperature and the reaction mixture stirred for 1.5 h. Next, the mixture was diluted with EtOAc (20 mL) and washed with saturated $NaHCO_3$ (3 × 20 mL). The organic phases were combined and dried over $MgSO_4$, and the solvent removed under reduced pressure. Compound **25** was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 1:2 as eluent, R_f = 0.30). Yield: 0.026 g (88%). ^{1}H NMR: $CDCl_3$, 300 MHz. δ (ppm): 7.33−7.26 (m, 2H), 7.04−6.79 (m, 5H), 6.50 (d, J = 16.0 Hz, 1H), 6.23 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.80 (s, 2H), 3.42 (dd, J = 6.5 Hz, J = 1.5 Hz, 2H). ^{13}C NMR: $CDCl_3$, 75 MHz. δ (ppm): 161.7 (d, J = 247.0 Hz, 1C), 148.8, 148.4, 135.8 (d, J = 3.0 Hz, 1C), 131.0, 129.9, 129.5 (d, J = 8.0 Hz, 1C), 126.1, 119.2, 114.9 (d, J = 21.0 Hz, 1C), 110.9, 108.4, 55.6, 55.5, 52.3, 51.0. IR (film, cm^{-1}): 2961, 2834, 1513, 1265, 1027, 824. MS(EI): 302 (M+H), 282, 178, 177. HRMS calcd for $C_{18}H_{21}FNO_2$ (M+H): 302.1551. Found: 302.1545.

(E)-Methyl 2-((3-(3,4-dimethoxyphenyl)allyl)(4-fluorobenzyl)amino)-acetate, ***2***.[39] Amine **25** (0.36 mmol, 0.113 g) and K_2CO_3 (0.79 mmol, 0.11 g) dissolved in 1 mL of CH_3CN were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under nitrogen. Next, KI (0.126 mmol, 0.021 g) and 2-chloroacetate (0.36 mmol, 0.040 g) were added to the reaction mixture and stirred for 24 h. After that time, the reaction mixture was diluted with EtOAc (10 mL) and washed with saturated $NaHCO_3$ (3 × 15 mL). The organic layers were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Compound **2** was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.55). Yield: 0.026 g (88%). ^{1}H NMR: $CDCl_3$, 500 MHz. δ (ppm): 7.36−7.30 (m, 2H), 7.03 (t, J = 8.5 Hz, 2H), 6.93−6.75 (m, 3H), 6.49 (d, J = 16.0 Hz, 1H), 6.15 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.76 (s, 2H), 3.66 (s, 3H), 3.39 (d, J = 6.5 Hz, 2H), 3.34 (s, 2H). ^{13}C NMR: $CDCl_3$, 125 MHz. δ (ppm): 171.7, 162.0 (d, J = 245.0 Hz, 1C), 148.9, 148.7, 134.2 (d, J = 3.0 Hz, 1C), 132.9, 130.5 (d, J = 8.0 Hz, 1C), 129.8, 124.8, 119.5, 115.1 (d, J = 21.0 Hz, 1C), 110.9, 108.5, 57.4, 56.4, 55.9, 55.7, 53.6, 51.4. MS(EI): 374 (M+1), 373 (M), 354, 264, 178, 177. HRMS calcd for $C_{21}H_{24}FNO_4$: 373.1689. Found: 373.1679.

(E)-Methyl-4-((3-(3,4-dimethoxyphenyl)allyl)(4-fluorobenzyl)amino)-butanoate, ***3***.[15] Amine **25** (0.06 g, 0.2 mmol), 4-oxobutanoate (0.025 g, 0.25 mmol), and THF (2 mL) were added to a flame-dried round-bottom flask equipped with a magnetic stir bar under a nitrogen. Next, $NaHB(OAc)_3$ (0.042 g, 0.2 mmol) was added, and the reaction mixture was stirred for 72 h at room temperature. After that time, the mixture was diluted with Et_2O (10 mL) and washed with saturated $NaHCO_3$ (3 × 15 mL). The organic layer were combined and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Compound **3** was obtained as oil after purification by flash chromatography (hexanes/ethyl acetate 7:3 as eluent, R_f = 0.67). Yield: 0.070 g (88%). ^{1}H NMR: $CDCl_3$, 500 MHz. δ (ppm): 7.24−7.19 (m, 2H), 6.95 (t, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 H, 2H), 6.73 (d, J = 8.5 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.01 (dt, J = 16.0 Hz, J = 6.5 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 3.54 (s, 3H), 3.49 (s, 2H), 3.11 (d, J = 6.5 Hz, 2H), 2.41 (t, J = 6.8 Hz, 2H), 2.27 (t, J = 7.30 Hz, 2H), 1.85 (q, J = 7.1 Hz, 2H). ^{13}C NMR: $CDCl_3$, 125 MHz. δ (ppm): 174.0, 163.4 (d, J = 245.0 Hz, 1C), 149.0, 148.8, 135.2 (d, J = 3.0 Hz, 1C), 132.2, 130.3 (d, J = 8.0 Hz, 1C), 130.1, 125.3, 119.3, 115.0 (d, J = 21.0 Hz, 1C), 111.0, 108.6, 57.4, 55.9, 55.9, 55.8, 52.3, 51.4, 31.7, 29.6. MS(CI): 401 (M), 292, 250, 178, 177, 109. HRMS calcd for $C_{23}H_{28}FNO_4$: 401.2002. Found: 401.1982.

■ ASSOCIATED CONTENT

Supporting Information. HPLC chromatographic analyses and preparative chromatographic separation of isomers **6e**, **7e**, and **8e** and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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