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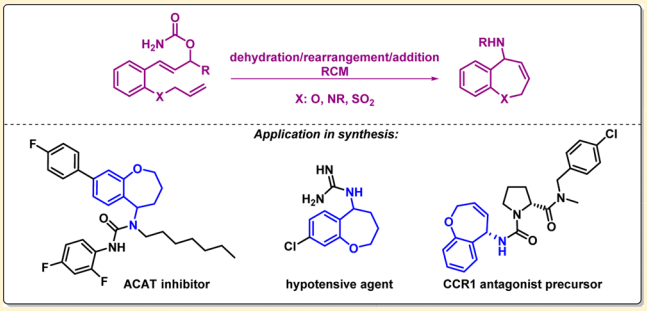
The Synthesis of 5-Amino-dihydrobenzo[*b*]oxepines and 5-Amino-dihydrobenzo[*b*]azepines via Ichikawa Rearrangement and Ring-Closing Metathesis

Monika Chwastek, Michał Pieczykolan, and Sebastian Stecko*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Supporting Information

ABSTRACT: The combination of Ichikawa's rearrangement and a ring-closing metathesis reaction of allyl carbamates is presented as a method for the preparation of 5-amino-substituted 2,5-dihydro-benzo[*b*]oxepines, 2,5-dihydro-benzo-[*b*]azepines, and 2,5-dihydro-benzo[*b*]thiepins. It was demonstrated that the use of nonracemic allyl carbamates enables the synthesis of enantioenriched benzo-fused seven-membered heterocycles. Finally, it was shown that further functionalization of the obtained structures allows access to pharmacologically active 5-amino-substituted 2,3,4,5-tetrahydro-1-benzo-[*b*]oxepine scaffolds.



INTRODUCTION

Benzannulated heterocycles constitute the core structure of numerous biologically active compounds which display a wide range of pharmacological activities.[1] One of the most important classes of this family are benzodiazepines and benzothiazepines, which have been established as highly valuable scaffolds for medicinal chemistry and drug development. Therefore, a lot of effort has been made in the past decades to develop efficient strategies for the synthesis of structurally diverse libraries of these molecules.[1−4]

In contrast, dihydro-1-benzoxepines and -benzazepines have received much less attention despite numerous reports on their interesting and promising bioactivity toward various targets. For example, radulanin A (**1**)[5] possesses antibiotic activity, whereas pterulone (**2**) is a fungal metabolite which inhibits eukaryotic respiration (Figure 1).[6] Another example is a group of benzoxepines which belong to the heliannuol family (**3**−**5**) and display allelopathic activity.[7] A large group of 1-benzazepines have been identified as nonpeptide vasopressin 2 receptor antagonists (Figure 2), for example, tolvaptan (**6**), and its analogues fedovapagon (**7**) and lixivaptan (**8**). Other structures have been reported to possess activity against enzymes (e.g., **9**),[8−15] ion channels (e.g., **10**),[16] and receptors.[17,18]

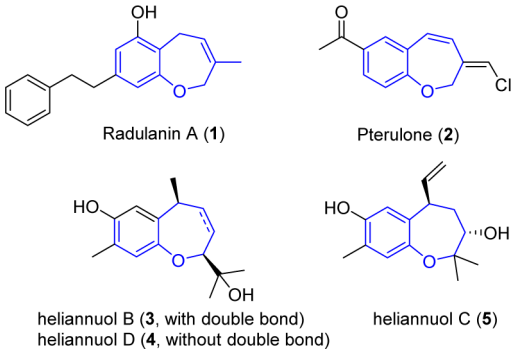


Figure 1. Structures of naturally occurring and biologically active 1-benzoxepines.

Among this class of biomolecules, 5-amino-1-benzoxepines and 5-aminobenzazepines are an interesting subgroup (Figure 3). For example, mozavaptan (**11**) and its analogues are nonpeptide vasopressin 2 receptor antagonists.[17a−f] Evacetrapib (**12**) is a potent cholesteryl ester transfer protein (CETP) inhibitor, which transfers and thereby increases HDL and lowers LDL levels, and as a result, may modify the risk of cardiovascular disease.[19] Other interesting examples are hypotensive agent **13**,[20] Src SH2 domain inhibitor **14**,[21] potassium channel activator **15**,[22] or acetyl-CoA cholesterol *O*-acyl transferase (ACAT) inhibitor **16**.[23,24]

Due to their widespread occurrence and extensive utilization as building blocks in pharmaceuticals, efficient and diversity-oriented synthetic protocols for the preparation of 1-benzoxepines and 1-benzazepines are highly desirable. Typical approaches involve the formation of the seven-membered ring,[1,25] for instance, by Friedel−Crafts type cyclization,[21] ring-closing metathesis,[26,27] transition-metal-catalyzed cyclizations,[28] or via substitution/condensation[29] and introduction of the amino function at the C-5 position, for example, via the Mitsunobu reaction,[21] allylic amination,[27] or imine allylation.[30] This also includes strategies based on the combination of the

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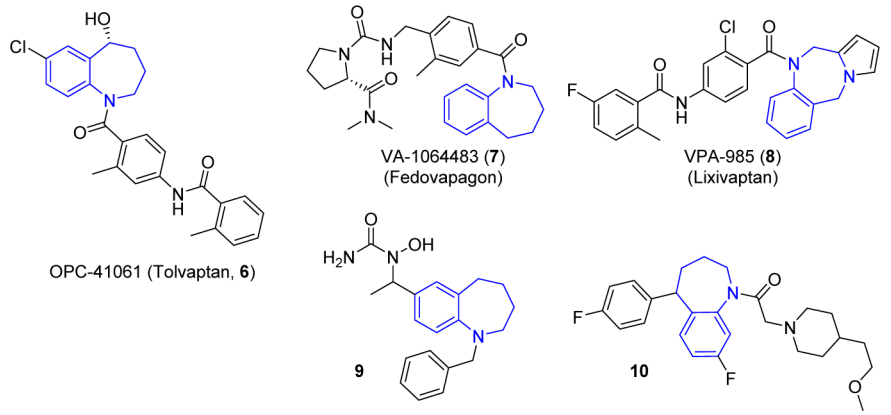


Figure 2. Structures of naturally occurring and biologically active 1-benzazepines.

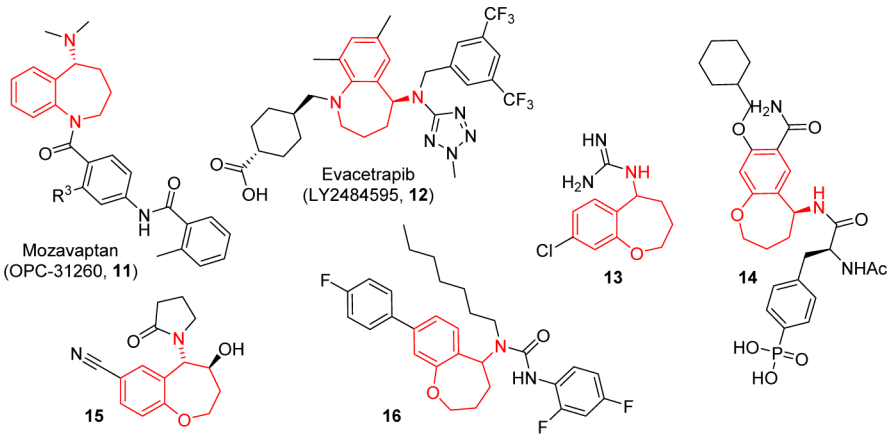
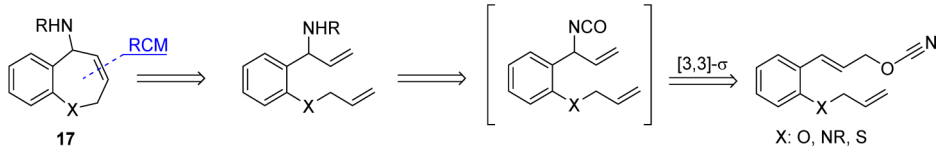


Figure 3. Structures of several biologically active 5-amino-substituted 1-benzoxepines and 1-benzazepines.

Scheme 1



Claisen rearrangement of allyl phenyl ethers, followed by *O*-allylation and a ring-closing metathesis (RCM) reaction, which have found numerous applications in the total synthesis of natural products.[5,31,26,32] Recently, Sutherland and co-workers have shown the use of Overman rearrangement/RCM in the synthesis of 5-amino-1-benzo[*b*]oxepines.[33] However, in this case, the rearrangement step requires harsh reaction conditions (reflux in xylene for 18−24 h[33]), which is a serious drawback of such an approach, especially for sensitive molecules.

Hence, as part of our program aimed at the application of cyanate-to-isocyanate rearrangement in the synthesis of biologically active molecules, we decided to ascertain whether this process, in combination with subsequent ring-closing metathesis, can be an attractive tool for the formation of benzo-fused seven-membered heterocycles—either benzoxepines or benzazepines (Scheme 1). It needs to be stressed that the transformation of the double bond in **17**, for example, through its hydrogenation or oxidation, should enable the access to a broad range of functionalized 5-amino-1-benzoxepine or 5-amino-1-benzazepine scaffolds present in a wide range of pharmacologically active compounds such as those presented in Figure 3.

RESULTS AND DISCUSSION

Synthesis of 5-Amino-dihydro-1-benzo[*b*]oxepines. Our efforts were primarily focused on developing efficient access to 5-amino-dihydro-1-benzoxepines. The study began with the preparation of a series of 2-allyloxy-cinnamyl carbamates **21a−n** which are direct precursors of allyl cyanates. Carbamates **21** were synthesized starting from easily available salicylaldehydes or salicylic acids which were converted into the corresponding allyl alcohols **20a−n** in high overall yields, as presented in Scheme 2. These alcohols were converted into allyl carbamates **21a−n** by treatment with trichloroacetyl isocyanate (TCAI) and subsequent hydrolysis. All of these compounds were obtained in high yields with one exception. Under the described conditions, carbamate **21i** was obtained with very poor yield which did not exceed 10%. This compound was quite unstable under the reaction conditions as well as during the further workup and purification. It was particularly surprising since other MeO-substituted carbamates

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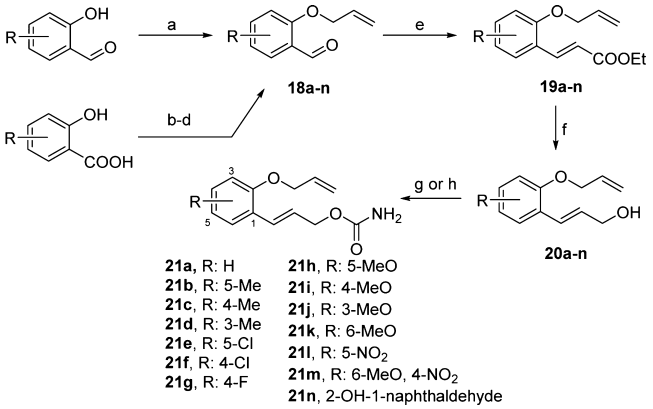
Scheme 2[a]



[a]Reagents and conditions: (a) allyl bromide, K_2CO_3, DMF, 70−90%; (b) in the case of the synthesis of carbamates **21f,g** and **k**: i. allyl bromide, K_2CO_3, DMF, 77−94%; (c) $LiAlH_4$, THF, −10 °C, 66−71%; (d) PCC, CH_2Cl_2, rt, 82−87%; (e) $(EtO)_2P(O)CH_2COOEt$, NaH, THF, rt, 80−96%; (f) DIBAL-H, CH_2Cl_2, −78 °C, 60−95%; (g) i. TCAI, CH_2Cl_2, rt, ii. aq. K_2CO_3, MeOH, rt, 60−96% (2 steps); (h) in the case of the synthesis of allyl carbamate **21i**: phenyl carbamate, dibutyltin maleate (20 mol %), PhMe, 90 °C, 50%.

(**20h**, **20j**, and **20k**) were synthesized and isolated without any problems.

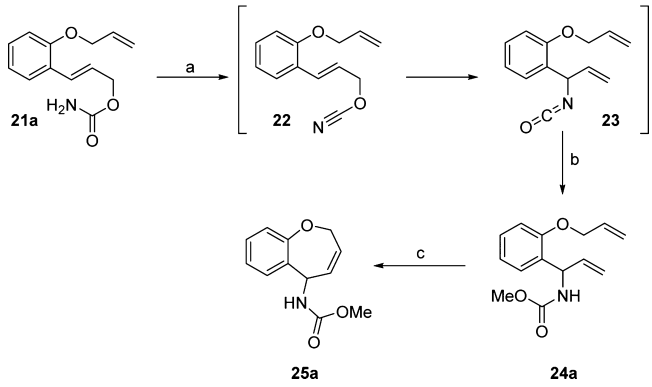
Modification of reaction conditions, such as lowering the reaction temperature or the addition of a tertiary amine, did not bring any improvement, neither did the change of the manner of isolation and purification. Finally, carbamate **21i** was prepared by using the Ichikawa's protocol.[34] Thus, alcohol **20i** was heated with phenyl carbamate in toluene in the presence of 20 mol % of dibutyltin maleate. After 3.5 h, complete conversion of the starting material was achieved and the product was isolated and chromatographed on florisil (50% yield). The reaction time was crucial in this case; its extension to 12 h resulted in significant decrease of the yield to ca. 35% along with increase of the amount of side products.

Carbamate **21a** was utilized as a model substrate for subsequent transformations. Its treatment with trifluoroacetic anhydride (TFAA) in the presence of Et_3N resulted in the formation of allyl cyanate **22**, which spontaneously underwent [3,3]-sigmatropic rearrangement to allyl isocyanate **23** (Scheme 3). The latter was not isolated but directly treated with MeOH in the presence of a catalytic amount of Bu_3SnOMe to provide carbamate **24a** in 90% overall yield after 3 steps.

Using the optimized conditions, we explored the scope of the investigated transformation (Scheme 4), and carbamates **21b**−**n** were subjected to the dehydration/rearrangement/addition sequence to provide the corresponding carbamates **23b**−**n**. The investigated approach was found to be general for various carbamates. As can be seen from the examples presented in Scheme 4, the rearrangement proceeded well for substrates bearing either electron-donating or electron-withdrawing groups. The location of the substituent in the phenyl ring, particularly of the same one, showed no significance in reactivity, giving the target products. In the case of isomeric products, the yields were comparable.

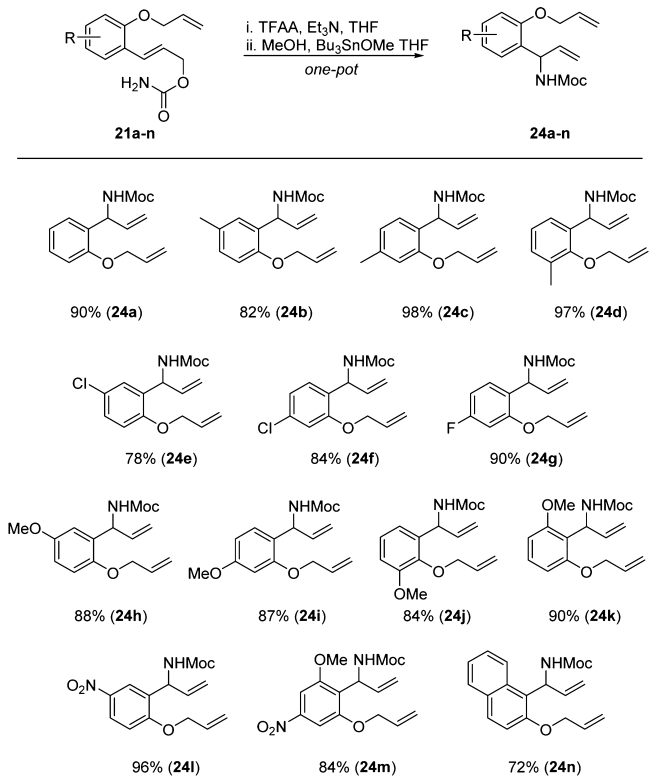
The formation of the isocyanate intermediate (e.g., **23**) during the rearrangement is a crucial advantage of the studied synthetic approach. Further derivatization of allyl isocyanates opens an access to a broad range of *N*-functionalized allylamines by using various nucleophilic agents. Moreover,

Scheme 3[a]



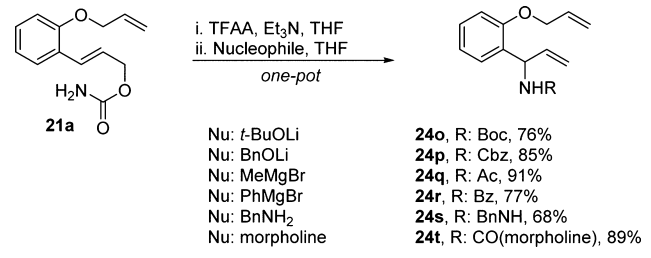
[a]Reagents and conditions: (a) TFAA, Et_3N, THF, 0 °C to rt, 1 h; (b) MeOH, Bu_3SnOMe, THF, rt, 90% (overall after 3 steps); (c) Grubbs II catalyst (5 mol %), DCE, 50 °C, 84%.

Scheme 4



the addition of the nucleophile to the isocyanate can be effected directly in a one-pot manner without its prior isolation (Scheme 5). Thus, the replacement of MeOH/Bu_3SnOMe by

Scheme 5



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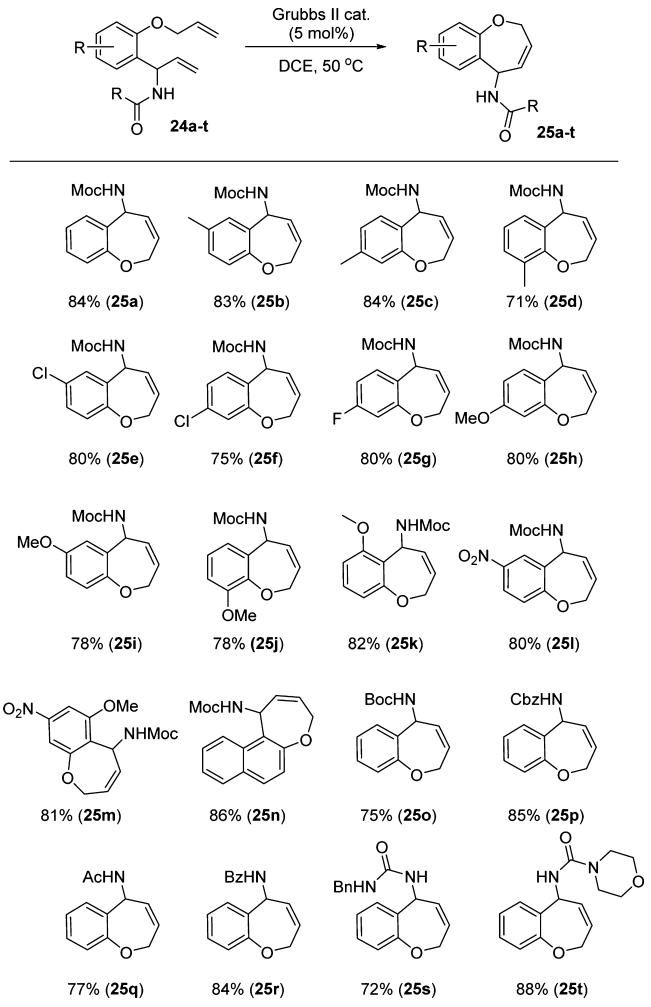
t-BuOLi or BnOLi enabled the synthesis of *N*-Boc- and *N*-Cbz-protected allylamines **24o** and **24p**, respectively. The isocyanate intermediate can be also trapped directly by a Grignard reagent to provide the corresponding amides, for instance, **24q** or **24r**. Finally, direct treatment of intermediate **23** with $BnNH_2$ or morpholine led to urea derivatives **24s** and **24t**.

In the final step, carbamates **24a−t** were subjected to the metathesis reaction to provide benzannulated products **25a−t**. The cyclization was performed in the presence of 5 mol % of the Grubbs II catalyst in dichloroethane at 50 °C (Scheme 6).

Scheme 6



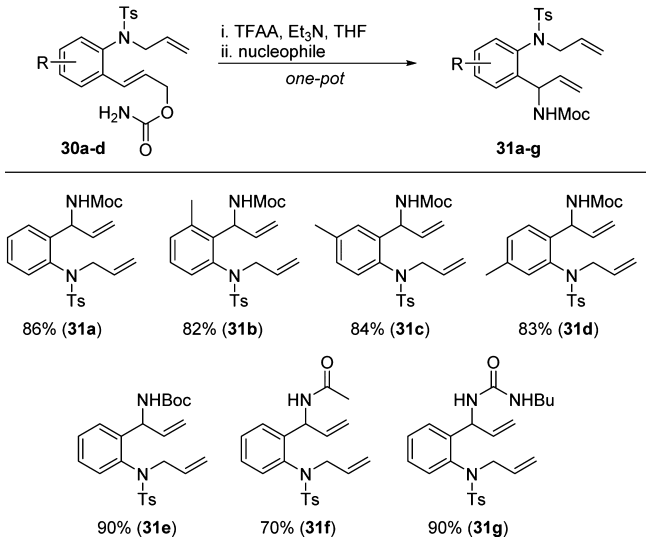
In most cases, the reaction proceeded smoothly and took 2−3 h until completion. Only the cyclization of urethanes **24s** and **24t** into benzoxepines **25s** and **25t**, respectively, required longer reaction time (ca. 6 h) and the addition of another portion of the catalyst after 3 h to achieve complete conversion of the starting material.

Synthesis of 5-Amino-1-benzo[*b*]azepines. Encouraged by the successful results of the synthesis of 5-amino-1-benzoxepines via the combination of the Ichikawa reaction and ring-closing metathesis, we decided to apply this approach to the synthesis of selected 5-amino-1-benzazepines.

Following the reaction sequence described above for benzoxepines, several carbamates of type **30** were prepared starting from 2-aminobenzaldehydes **26a−e**, as shown in Scheme 7.

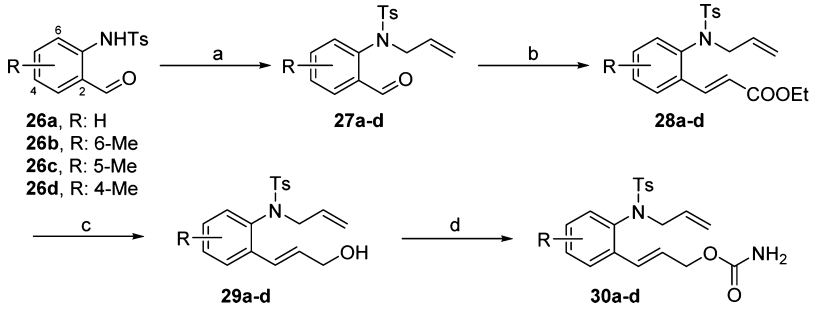
Their treatment with TFAA/Et_3N, followed by the addition of MeOH/Bu_3SnOMe, provided the desired rearrangement products (**31a−d**) with high overall yields after 3 steps (Scheme 8). This process proceeded efficiently also when other nucleophilic agents were used to trap the isocyanate intermediate (**31e−g**).

Scheme 8



Finally, dienes **31a−g** were subjected to the ring-closing metathesis reaction under the previously described conditions

Scheme 7[a]



[a]Reagents and conditions: (a) allyl bromide, NaH, DMF, rt; (b) $(EtO)_2P(O)CH_2COOEt$, NaH, THF, rt; (c) DIBAL-H, CH_2Cl_2, −78 °C; (d) i. TCAI, CH_2Cl_2, rt, ii. aq. K_2CO_3, MeOH, rt.

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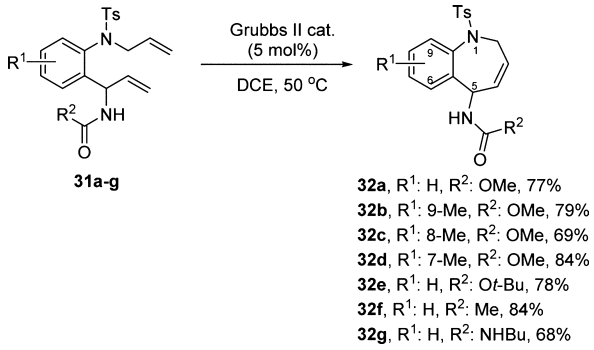
to provide the corresponding 5-amino-benzazepines **32a–g** with good yields (Scheme 9).

Scheme 9



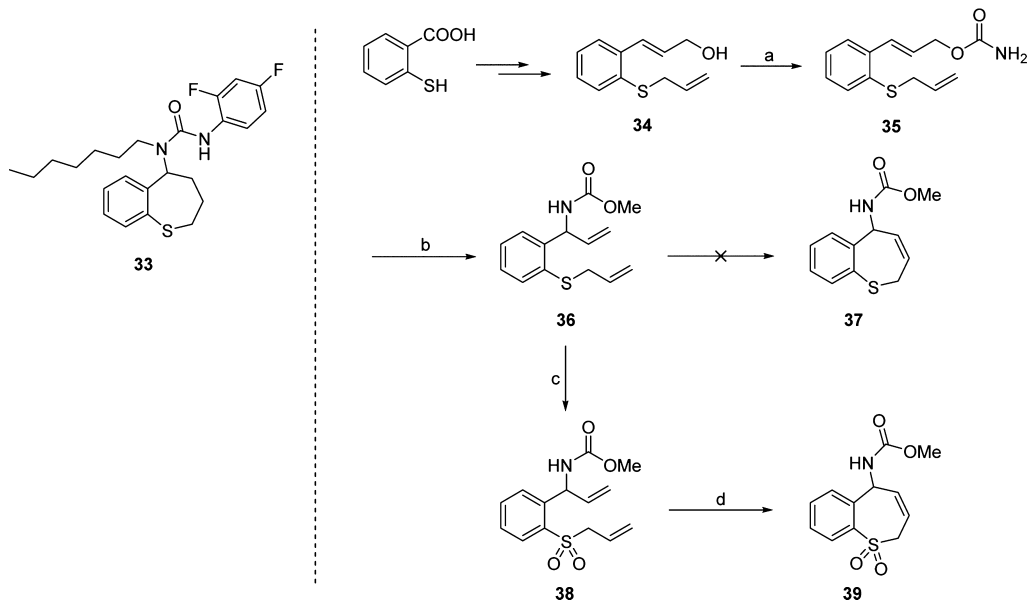
In 1995, Festal and co-workers reported that sulfur analogues of 5-amino-benzoxepine **16** are also potential ACAT inhibitors (e.g., **33**).[24] This inspired us to examine whether the studied Ichikawa rearrangement/RCM approach may be applied in the synthesis of the 5-amino-benzo[*b*]thiepin scaffold. For this purpose, thiosalicylic acid derived allyl alcohol **34** was converted into allyl carbamate **35**. This compound was rearranged to **36** in 73% yield under standard conditions (Scheme 10). Unfortunately, despite many attempts, the final ring-closing metathesis reaction catalyzed by the Grubbs II catalyst under various conditions failed. The replacement of the Grubbs II catalyst by other ruthenium complexes also did not bring any change. Each time, only the starting material was observed along with slight amounts of decomposition products.

To overcome this problem, the sulfur atom in **36** was selectively oxidized to sulfone **38**. Now, the ring-closing metathesis reaction proceeded smoothly and provided the desired bicyclic product **39** in 90% yield (Scheme 10). It would be expected that the sulfone moiety in **39** could be reduced to the sulfide by known procedures.[35]

Synthesis of Nonracemic 5-Amino-1-benzoxepines and 5-Amino-1-benzazepines. In a continuation of our studies, we focused our interests on the synthesis of nonracemic 5-amino-1-benzoxepines and 5-amino-1-benzazepines. Since the Ichikawa rearrangement is a spontaneous noncatalytic process, it cannot be performed in an enantioselective fashion by the use of a chiral transition metal complex as is possible in the case of an asymmetric Overman rearrangement.[36] However, due to the concerted course of the sigmatropic transformation proceeding through a cyclic transition state, stereoselective generation of a new stereogenic center can be achieved by efficient chirality transfer. This can be accomplished when a nonracemic starting allyl carbamate is applied.[37] Very recently, we have shown that such an approach is a very useful tool for the preparation of enantiomerically enriched allylamines[38] and, therefore, decided to use the same approach in the current studies (Scheme 11).

Our efforts were primarily focused on the synthesis of the required type **40** nonracemic allyl alcohols. Initially, an asymmetric reduction of model enone **41** to allyl alcohol **42** was investigated (Table 1). The CBS reduction of **41** with BH_3·Me_2S in the presence of (*S*)-2-methyl-CBS-oxazaborolidine provided (***R***)-**42** in poor 40% yield (complete conversion of starting material) and with low enantioselectivity (*ee* 43%). The decrease of reaction temperature did not improve the level of the selectivity but suppressed the reduction. The replacement of borane with catecholborane gave only traces of the desired product. Asymmetric hydrogenation of **41** with hydrogen in the presence of a Noyori-type catalyst (entry 3)[39] resulted in complete decomposition of the starting material. Alterative asymmetric hydrogen transfer reduction of **41** catalyzed by the Ru(*p*-cymene)(*S*,*S*)-Ts-DPEN[40] complex again gave only traces of the desired product (Table 1, entry 4). Alcohol (***S***)-**42** was obtained in 43% yield (*ee* 50%, entry 5) when the HCOOH:Et_3N (5:2) complex was applied as the hydrogen

Scheme 10[a]



[a]Reagents and conditions: (a) i. TCAI, CH_2Cl_2, rt; ii. aq. K_2CO_3, MeOH, rt, 81% (2 steps); (b) i. TFAA, Et_3N, THF; ii. Bu_3SnOMe (10 mol %), MeOH, 73% (3 steps); (c) *m*-CPBA, CH_2Cl_2, rt, 81%; (d) Grubbs II cat. (5 mol %), DCE, 50 °C, 90%.

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Scheme 11

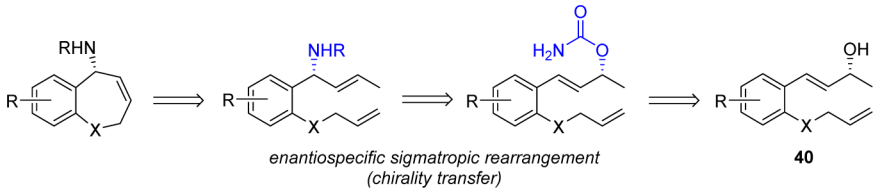
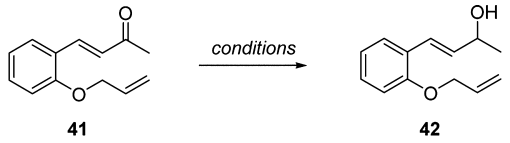


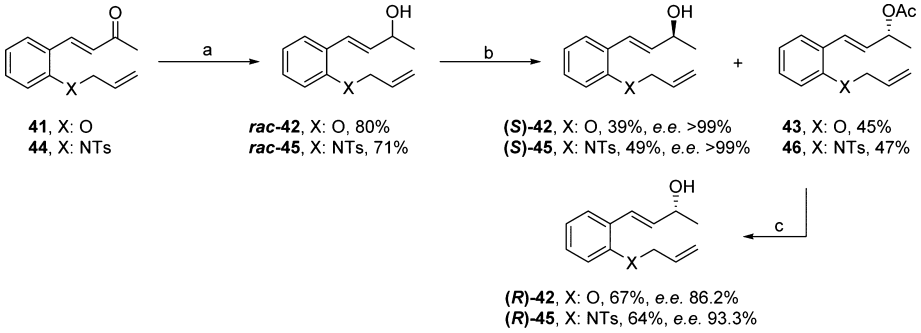
Table 1. Asymmetric Reduction of Enone 41



entry	method	yield [%]	*ee*[a] [%]
1	(*S*)-Me-CBS, $BH_3{\cdot}Me_2S$, −30 °C, THF, 14 h	40	43(*R*)
2	(*S*)-Me-CBS, catecholborane, −30 °C, THF, 14 h	traces	
3	$RuCl_2$[(*S*)-DM-BINAP)][(*S*,*S*)-DPEN], H_2 (15 bar), *i*-PrOH	*dc*	
4	RuCl(*p*-cymene)(*S*,*S*)-Ts-DPEN (10 mol %), KOH (10 mol %), *i*-PrOH, rt	traces	
5	RuCl(*p*-cymene)(*S*,*S*)-Ts-DPEN (10 mol %), HCOOH-Et_3N (5:2), CH_2Cl_2, rt	43	50(*S*)
6	$Zn(OAc)_2$ (5 mol %), ligand, DEMS, THF, 25 °C	*nr*	
7	$Cu(OAc)_2$ (3 mol %), (*R*)-DTBM-SEGPHOS (3 mol %), DEMS, Et_2O, −25 °C	traces	
8	(*S*)-BINAL-H, THF, −78 °C to rt, 12 h	60	68(*R*)

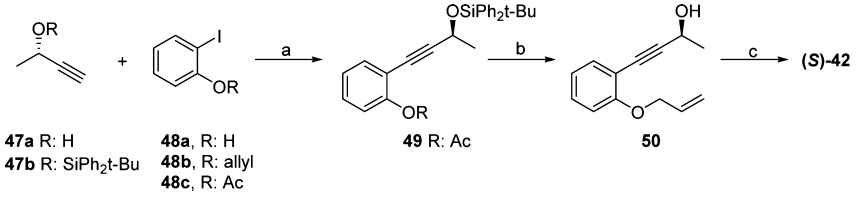
[a]Determined by HPLC: Chiralpak OD-H, 10% IPA/hexanes, 1 mL/min, 254 nm; R_t 15.9 min (*R* isomer) and 27.4 min (*S* isomer). *nr* = no reaction; *dc* = decomposition of starting material.

Scheme 12[a]



[a]Reagents and conditions: (a) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, MeOH, rt; (b) vinyl acetate, *Candida antarctica* lipase, pentane, MS 4 Å, rt; (c) K_2CO_3, $MeOH/H_2O$ (4:1), rt.

Scheme 13[a]



[a]Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$ (1 mol %), CuI (10 mol %), Et_3N, THF, rt, 84%; (b) i. NH_3, MeOH, rt, ii. allyl bromide, K_2CO_3, DMF, iii. TBAF, THF, rt, 62% (3 steps); (c) $LiAlH_4$, THF, rt, 85%.

source.[41] The reduction of **41** with $(EtO)_2MeSiH$ in the presence of a chiral copper complex, according to Lipshutz's protocol,[42] gave only traces of the desired alcohol. An analogous reaction catalyzed by a chiral zinc complex[43] failed, and only starting material was recovered. Stoichiometric reduction with BINAL-H[44] was more efficient but still provided the desired product in moderate 60% yield, and the enantiomeric enrichment was not sufficient for further purposes.

The low efficiency of the synthesis of nonracemic alcohol **42** forced us to change the planned strategy of its preparation. Thus, enone **41** was reduced with $NaBH_4/CeCl_3$ to provide ***rac*-42**. This alcohol was subjected to a kinetic resolution reaction by treatment with vinyl acetate in the presence of

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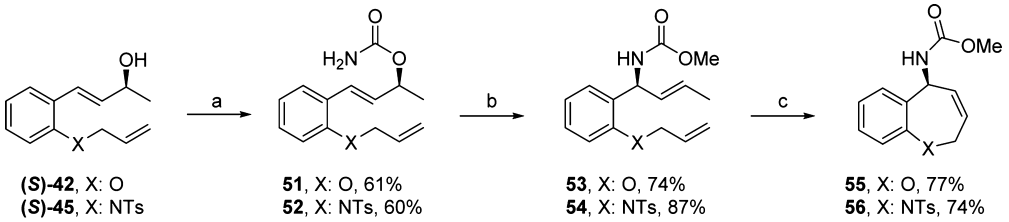
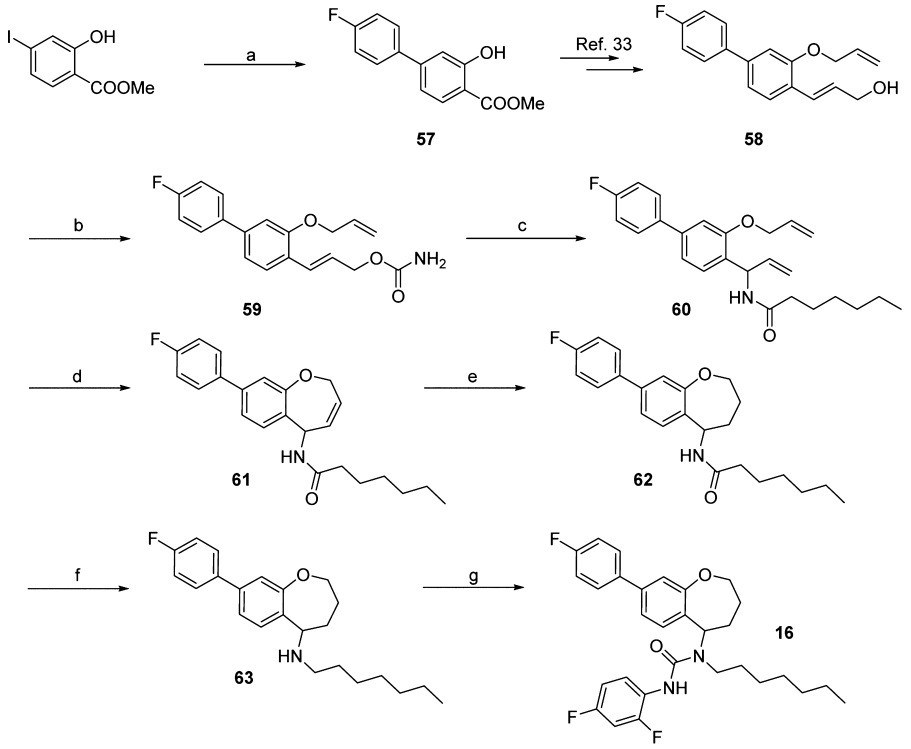
Scheme 14[a]



[a]Reagents and conditions: (a) phenyl carbamate, dibutyltin maleate (20 mol %), PhMe, 90 °C; (b) i. TFAA, Et_3N, THF, 0 °C to rt, 1 h; ii. Bu_3SnOMe (10 mol %), MeOH, rt; (c) Grubbs II cat. (5 mol %), DCE, 50 °C.

Scheme 15[a]



[a]Reagents and conditions: (a) 4-fluorophenylboronic acid, $Pd(dppf)Cl_2$ (5 mol %), Cs_2CO_3 (2 equiv), 1,4-dioxane/H_2O, 80 °C, 14 h, 85%; (b) i. TCAI, CH_2Cl_2, rt, ii. aq. K_2CO_3, MeOH, rt, 79% (2 steps); (c) i. TFAA, Et_3N, THF, 0 °C to rt, 1 h; ii. *n*-hexylMgBr, THF, 0 °C to rt, 6 h, 70% (overall after 3 steps); (d) Grubbs II cat. (3 mol %), DCE (*c* 0.01M), 86%; (e) H_2, 10% Pd/C, AcOEt, 96%; (f) $LiAlH_4$, THF, 60 °C; (g) 2,4-difluorophenyl isocyanate, THF, rt, 73%.

Candida antarctica lipase to afford (*S*)-**42** along with (*R*)-acetate **43** (Scheme 12). The latter was next hydrolyzed to furnish alcohol (*R*)-**42**. Both isomers were obtained with a good level of enantioselectivity. In the same manner, nitrogen analogues (*S*)-**45** and (*R*)-**45** were prepared (Scheme 12).

Independently, an alternative approach to nonracemic alcohol **42**, which is outlined in Scheme 13, was investigated. The new concept assumed coupling of 2-iodophenol (**48a**) with commercially available (*S*)-but-3-yn-2-ol (**47a**), but only traces of the desired product was obtained. Better results were obtained in the case of the coupling reaction of **47a** with *O*-protected 2-iodophenol **48b**; desired product **50** was obtained in 30% yield only. The coupling proceeded more efficiently when both *O*-protected starting marerials **47b** and **48c** were applied (84%). The product **49** was then deacetylated by treatment with NH_3 in MeOH, *O*-allylated and desilylated to provide **50** in 62% overall yield. Finally, hydroalumination of the triple bond with $LiAlH_4$, followed by hydrolysis, gave (*S*)-**42** in 85% yield (96.7% *ee*). This synthetic approach let us also to confirm the absolute configuration of alcohols **42** obtained by a kinetic resolution.

With nonracemic allyl alcohols in hand, we prepared the corresponding allyl carbamates **51** and **52** by tin-catalyzed transcarbamoylation with phenyl carbamate (Scheme 14).[34] The previously used protocol based on treatment with TCAI gave the desired carbamates **51** and **52** with lower yields (ca. 30−40%). Their sequential dehydration/rearrangement/addition transformation provided compounds **53** and **54**, which were subjected to the final cyclization step. The RCM reaction catalyzed by the Grubbs II catalyst gave the desired chiral benzannulated seven-membered heterocycles **55** and **56** in 77% and 74% yields, respectively (Scheme 14).

Application of the Ichikawa Rearrangement/RCM Sequence to the Synthesis of Bioactive Molecules. The final step of this research program was the demonstration of the

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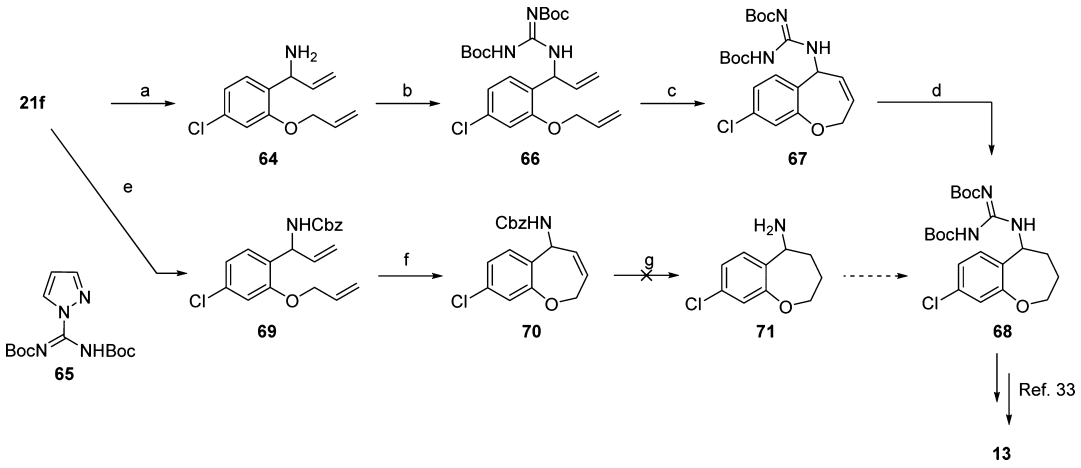
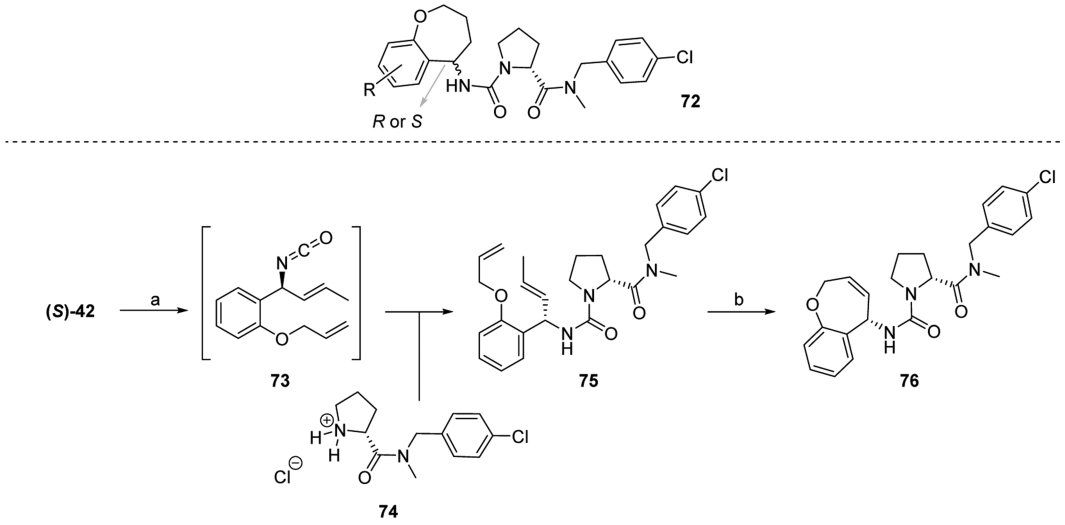
Scheme 16[a]



[a]Reagents and conditions: (a) i. TFAA, Et_3N, THF, 0 °C, 1 h; ii. TMSOLi, THF, rt, 3 h; iii. TBAF, THF, rt, 73% (4 steps); (b) **65**, DMF, rt, 72%; (c) Grubbs II catalyst (2 × 3 mol %), DCE, 60 °C, 77%; (d) H_2, $Pd(OH)_2$, AcOEt, rt, 1.5 h, 88%; (e) i. TFAA, Et_3N, THF, 0 °C, 1 h; ii. BnOLi, THF, rt, 93% (overall after 3 steps); (f) Grubbs II catalyst (5 mol %), DCE, 64%; (g) H_2, 10% Pd/C, AcOEt, rt.

Scheme 17[a]



[a]Reagents and conditions: (a) TFAA, Et_3N, THF, 0 °C, 1 h; ii. amine **74**, Et_3N, THF, 65% (3 steps); (b) Grubbs II catalyst (5 mol %), DCE, 76%.

synthetic utility of the developed approach in the synthesis of biologically active scaffolds.

The already mentioned cholesterol *O*-acyl transferase (ACAT) is an enzyme which plays an important part in intracellular cholesterol esterification, for instance, in the intestines or liver.[24] Its inhibitors are expected to prevent both hypercholesterolemia and atherosclerosis. Among structurally different potential ACAT inhibitors, seven-membered heterocycles can be found, for instance, the already mentioned 5-amino-benzoxepine **16**. We decided to apply the reported synthetic protocol in the total synthesis of compound **16**. For this purpose, allyl alcohol **58** was prepared by modifying the previously reported protocol starting from methyl 4-iodosalicylate and 4-fluorophenylboronic acid (Scheme 15).[33b] Alcohol **58** was treated with TCAI, followed by basic hydrolysis, to give allyl carbamate **59**. Compound **59** was then treated with TFAA in the presence of Et_3N to provide the corresponding isocyanate. This was directly treated with *n*-hexylmagnesium bromide to afford carbamate **60** in 70% yield after 3 steps. In this manner, the side chain of the target compound was directly established. In the next step, diene **60** was treated with the Grubbs II catalyst to afford ring-closing metathesis product **61** in 86% yield. Then, the double bond in **61** was hydrogenated (**62**), followed by the reduction of the amide function by $LiAlH_4$. The resulting amine **63**, after simple aqueous workup, was directly treated with 2,4-difluorophenyl isocyanate to provide the final product **16** in 73% yield (Scheme 15).

Another interesting target was guanidine derivative **13**, a hypotensive agent.[20] To obtain the target **13**, carbamate **21f** was subjected to the Ichikawa domino process (Scheme 16). The isocyanate intermediate was trapped with TMSOLi, followed by treatment with TBAF, to provide free allylamine **64**.[45] Guanylation of **64** with di-Boc-pyrazole-1-carboximidamide (**65**)[46,33b] gave guanidine derivative **66** in 72% yield. This compound was then subjected to Grubbs II complex catalyzed RCM reaction to provide the corresponding cyclic product **67** in 77% yield. Hydrogenation of the double bond in **67** in the presence of the $Pd(OH)_2$ (10 mol %) provided

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product **68** (88%), which can serve as a direct precursor of hypotensive agent **13** (Scheme 16).[33b]

We also investigated an alternative approach in which the guanylation was planned to be performed at the late stages of the synthesis after the formation of the oxepine ring (Scheme 16). Thus, compound **21f** was transformed into *N*-Cbz allylamine **69** (93% after 3 steps). In the presence of the Grubbs II catalyst, it was cyclized to compound **70** in 64% yield. In the next step, simultaneous hydrogenation of the double bond and deprotection of the amine function to give amine **71** were planned. Disappointingly, the hydrogenation in the presence of Pd/C or $Pd(OH)_2$ resulted in dehalogenation and partial degradation of the seven-membered ring.

Finally, the presented approach can also be applied in the synthesis of compounds such as **72** which show activity as CCR1 antagonists (Scheme 17).[47] As shown in Scheme 17, the treatment of the isocyanate intermediate **73** generated from carbamate **(*S*)-42** with proline amide **74**,[47] provided the product **75** in 65% yield. Upon treatment with the Grubbs II catalyst, diene **75** was cyclized to product **76** (76%). Further transformation of **76** should provide **72**-type molecules (Scheme 17). In addition, the use of **(*R*)-42**, following the same reaction sequence, should open access to their diastereoisomeric forms.

CONCLUSIONS

In summary, a general method for the preparation of 5-amino-2,5-dihydro-1-benzoxepines, -azepines, and -thiepins was reported. The presented approach is based on a one-pot dehydration/rearrangement/addition reaction sequence (Ichikawa rearrangement), followed by the ring-closing metathesis reaction of readily available 2-allyloxy-, *N*-Ts-2-allylamino-, or 2-allylthio-cinnamyl carbamate derivatives. These starting materials can be easily prepared from readily available 2-hydroxy-, 2-amino-, or 2-mercapto-benzaldehydes. The presented method allows the preparation of diverse libraries of 5-amino benzannulated seven-membered heterocycles.

The reported approach is complementary to the previously reported[33b] method of preparation of 5-amino-2,5-dihydro-1-benzoxepines via the Overman rearrangement/RCM sequence. However, the use of the Ichikawa reaction has several significant advantages. In contrast to the Overman reaction, this transformation proceeds under milder conditions (at 0 °C/rt for 1 h vs reflux in xylene for 18−24 h[33b]) and does not require any catalyst. The utility of the Ichikawa reaction as a key step enables the direct formation of *N*-functionalized allylamines in a one-pot manner by trapping the intermediate isocyanate by selected nucleophilic agents. The use of nonracemic starting allyl carbamates, which can be prepared either by enzymatic kinetic resolution or by coupling reaction, enables the access to enantiomerically enriched heterocycles. Finally, the synthetic utility of the reported approach was illustrated by the synthesis of selected biologically active 5-amino-1,2,3,4-tetrahydrobenzo[*b*]oxepines.

EXPERIMENTAL SECTION

Allylation of Salicylaldehydes. General Procedure. To a stirred solution of salicylaldehyde (1 equiv) in anhydrous DMF (0.7 M) were added anhydrous K_2CO_3 (1.5 equiv) and allyl bromide (1.5 equiv). The resulting mixture was stirred until complete consumption of the starting material was achieved, as determined by TLC. The postreaction mixture was then diluted with AcOEt and washed with water (3×) and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness *in vacuo*. The product was isolated by flash column chromatography using AcOEt/hexanes mixtures as the eluent.

2-(Allyloxy)benzaldehyde (18a). Yield 15.75 g (78%) starting from 15 g of salicylaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.48 (s, 1H), 7.81−7.71 (m, 1H), 7.52−7.42 (m, 1H), 7.00−6.86 (m, 2H), 6.09−5.96 (m, 1H), 5.44−5.36 (m, 1H), 5.31−5.24 (m, 1H), 4.70−4.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.5, 160.9, 135.80, 135.79, 132.4, 128.3, 125.1, 120.8, 117.9, 112.9, 69.1; FTIR (film) ν: 2922, 2856, 1687, 1599, 1488, 1457, 1396, 1286, 1241, 1224, 1162, 995, 843, 758 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{10}O_2$ [M] 162.0681; Found 162.0687.

2-(Allyloxy)-5-methylbenzaldehyde (18b). Yield 6.29 g (99%) starting from 5 g of 5-methylsalicylaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.46 (s, 1H), 7.58 (d, *J* 2.4 Hz, 1H), 7.27 (ddd, *J* 8.5, 2.4, 0.6 Hz, 1H), 6.83 (d, *J* 8.5 Hz, 1H), 6.02 (ddt, *J* 17.3, 10.4, 5.1 Hz, 1H), 5.40 (dq, *J* 17.3, 1.7 Hz, 1H), 5.27 (dq, *J* 10.6, 1.4 Hz, 1H), 4.57 (dt, *J* 5.2, 1.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.7, 159.0, 136.4, 132.6, 130.2, 128.3, 124.8, 117.8, 112.9, 69.2, 20.2; FTIR (film) ν: 2923, 2861, 2760, 1685, 1612, 1495, 1285, 1247, 1162, 1018, 996, 940, 812, 731 cm^{-1}; HRMS (EI) m/z calcd for $C_{11}H_{12}O_2$ [M] 176.0837; Found 176.0842.

2-(Allyloxy)-4-methylbenzaldehyde (18c). Yield 6.65 g (77%) starting from 6.65 g of 4-methylsalicylaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.43 (d, *J* 0.8 Hz, 1H), 7.69 (d, *J* 7.9 Hz, 1H), 6.82−6.77 (m, 1H), 6.74 (s, 1H), 6.04 (ddt, *J* 17.3, 10.4, 5.1 Hz, 1H), 5.42 (dq, *J* 17.3, 1.7 Hz, 1H), 5.30 (dq, *J* 10.6, 1.4 Hz, 1H), 4.60 (dt, *J* 5.1, 1.6 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.2, 161.0, 147.3, 132.5, 128.3, 122.9, 121.8, 117.8, 113.4, 69.0, 22.3; FTIR (film) ν: 3077, 3020, 2985, 2923, 2859, 2762, 1683, 1606, 1418, 1258, 814 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}O_2Na$ [M + Na$^+$] 199.0735; Found 199.0734.

2-(Allyloxy)-3-methylbenzaldehyde (18d). Yield 6.16 g (95%) starting from 5 g of 3-methylsalicylaldehyde; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.36 (d, *J* 0.7 Hz, 1H), 7.67 (dd, *J* 7.7, 1.3 Hz, 1H), 7.43 (ddd, *J* 7.5, 1.8, 0.7 Hz, 1H), 7.12 (t, *J* 7.6 Hz, 1H), 6.09 (ddt, *J* 17.1, 10.4, 5.7 Hz, 1H), 5.41 (dq, *J* 17.1, 1.5 Hz, 1H), 5.32−5.26 (m, 1H), 4.45 (dt, *J* 5.7, 1.3 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ: 190.4, 160.4, 137.5, 132.7, 132.4, 129.5, 126.3, 124.4, 118.6, 76.5, 15.8; FTIR (film) ν: 3080, 3017, 2981, 2923, 2860, 27, 52, 1695, 1682, 1589, 1470, 1391, 1248, 1203, 1085, 986, 921, 783, 768 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}O_2Na$ [M + Na$^+$] 199.0735; Found 199.0737.

2-(Allyloxy)-5-chlorobenzaldehyde (18e). Yield 5.96 g (95%) starting from 5 g of 5-chlorosalicylaldehyde; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.44 (s, 1H), 7.77 (d, *J* 2.7 Hz, 1H), 7.45 (dd, *J* 8.9, 2.8 Hz, 1H), 6.92 (d, *J* 8.9 Hz, 1H), 6.05 (ddt, *J* 17.2, 10.5, 5.2 Hz, 1H), 5.43 (dq, *J* 17.3, 1.5 Hz, 1H), 5.34 (dq, *J* 10.6, 1.5 Hz, 1H), 4.64 (dt, *J* 5.2, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.3, 159.3, 135.3, 132.0, 127.9, 126.6, 126.0, 118.5, 114.6, 69.6; FTIR (film) ν: 1685, 1596, 1480, 1393, 1271, 1181 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{13}O_3ClNa$ [M + MeOH + Na$^+$] 251.0451; Found 251.0448.

2-(Allyloxy)-5-methoxybenzaldehyde (18h). Yield 5.95 g (94%) starting from 5 g of 5-methoxysalicylaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.49 (s, 1H), 7.32 (d, *J* 3.3 Hz, 1H), 7.10 (dd, *J* 9.1, 3.3 Hz, 1H), 6.93 (d, *J* 9.1 Hz, 1H), 6.05 (ddt, *J* 17.2, 10.5, 5.2 Hz, 1H), 5.42 (dq, *J* 17.3, 1.6 Hz, 1H), 5.31 (dq, *J* 10.5, 1.4 Hz, 1H), 4.60 (dt, *J* 5.2, 1.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.5, 155.7, 153.8, 132.6, 125.4, 123.4, 118.0, 114.9, 110.3, 70.0, 55.8; FTIR (film) ν: 3079, 3001, 2941, 2910, 2864, 2837, 1686, 1494, 1425, 1394, 1279, 1217, 1162, 1039, 935, 815, 724, 587 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}O_3Na$ [M + Na$^+$] 215.0684; Found 215.0682.

2-(Allyloxy)-4-methoxybenzaldehyde (18i). Yield 6.09 g (96%) starting from 5 g of 4-methoxysalicylaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.31 (s, 1H), 7.77 (d, *J* 8.7 Hz, 1H), 6.53−6.48 (m, 1H), 6.40 (d, *J* 2.2 Hz, 1H), 6.03 (ddt, *J* 17.3, 10.5, 5.1 Hz, 1H), 5.42 (dq, *J* 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* 10.5, 1.4 Hz, 1H), 4.61−4.56 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.1, 166.0,

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162.6, 132.3, 130.4, 119.2, 118.0, 106.1, 99.0, 69.1, 55.6; FTIR (film) ν: 3082, 3010, 2940, 2854, 2766, 1678, 1602, 1502, 1442, 1294, 1261, 1201, 1171, 1114, 1004, 824 cm^{-1}; HRMS (ESI-TOF) m/z calcd $C_{11}H_{12}O_3Na$ [M + Na^+] 215.0686; Found 215.0676.

2-(Allyloxy)-3-methoxybenzaldehyde (18j). Yield 5.73 g (85%) starting from 5 g of 3-methoxysalicylaldehyde; colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 10.44 (s, 1H), 7.41 (dd, J 7.3, 2.1 Hz, 1H), 7.17−7.10 (m, 2H), 6.07 (ddt, J 16.5, 10.4, 6.1 Hz, 1H), 5.38−5.33 (m, 1H), 5.28−5.24 (m, 1H), 4.66 (d, J 6.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 190.3, 152.9, 151.1, 133.1, 130.1, 124.0, 118.9, 118.7, 117.9, 75.1, 55.9; FTIR (film) ν: 3084, 3011, 2941, 2863, 1692, 1584, 1481, 1267, 1250, 1066, 983, 786 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{12}O_3Na$ [M + Na^+] 215.0684; Found 215.0678.

2-(Allyloxy)-5-nitrobenzaldehyde (18l). Yield 6.12 g (98%) starting from 5 g of 5-nitro-salicylaldehyde; white solid; mp 61−62 °C (Lit.[33b] 62−64 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 10.50 (s, 1H), 8.71 (d, J 2.9 Hz, 1H), 8.41 (dd, J 9.2, 2.9 Hz, 1H), 7.11 (d, J 9.2 Hz, 1H), 6.09 (ddt, J 17.3, 10.5, 5.3 Hz, 1H), 5.49 (dq, J 17.3, 1.6 Hz, 1H), 5.43 (dq, J 10.6, 1.3 Hz, 1H), 4.80 (dt, J 5.3, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.4, 164.6, 141.7, 131.0, 130.5, 124.9, 124.7, 119.5, 113.3, 70.2; FTIR (film) ν: 3357, 3096, 2880, 1685, 1609, 1526, 1348, 1278, 1178, 988, 924, 835, 747 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_9NO_4$ [M] 207.0518; Found 207.0520.

2-(Allyloxy)-6-methoxy-4-nitrobenzaldehyde (18m). Yield 5.9 g (98%) starting from 5 g of 6-methoxy-4-nitro-salicylaldehyde; white solid, mp 82−83 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 10.35 (s, 1H), 7.63 (d, J 3.3 Hz, 1H), 7.57 (d, J 3.3 Hz, 1H), 6.13−6.00 (m, 1H), 5.39 (dq, J 17.1, 1.4 Hz, 1H), 5.34 (dq, J 10.3, 1.0 Hz, 1H), 4.61 (dt, J 6.1, 1.2 Hz, 3H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 187.7, 155.5, 148.4, 144.8, 132.2, 131.6, 120.5, 117.1, 116.6, 79.1, 56.3; FTIR (film) ν: 3083, 2974, 2949, 2886, 2844, 1688, 1534, 1427, 1348, 1305, 1233, 1049, 945, 928, 784 cm^{-1}; HRMS (EI) m/z calcd for $C_{11}H_{11}NO_5$ [M] 237.0637; Found 237.0636.

2-(Allyloxy)-1-naphthaldehyde (18n). Yield 3.57 g (58%) starting from 5 g of 2-hydroxy-1-naphylaldehyde; yellow solid, mp 73−74 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 9.30−9.26 (m, 1H), 8.00 (d, J 9.1 Hz, 1H), 7.75 (d, J 8.1 Hz, 1H), 7.61 (ddd, J 8.5, 6.9, 1.4 Hz, 1H), 7.41 (ddd, J 8.1, 6.9, 1.1 Hz, 1H), 7.23 (d, J 9.2 Hz, 1H), 6.09 (ddt, J 17.3, 10.4, 5.2 Hz, 1H), 5.47 (dq, J 17.3, 1.7 Hz, 1H), 5.35 (dq, J 10.6, 1.4 Hz, 1H), 4.77 (dt, J 5.2, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 192.0, 192.0, 163.1, 132.3, 131.5, 129.8, 128.6, 128.2, 125.0, 124.8, 118.3, 117.2, 113.9, 70.2; FTIR (film) ν: 2928, 2883, 2871, 1661, 1592, 1514, 1340, 1268, 1244, 1151, 1053, 1024, 1008, 955, 808, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{12}O_2$ [M] 212.0837; Found 212.0835.

Allyl 2-(Allyloxy)-4-fluorobenzoate. To a stirred solution of 4-fluorosalicylic acid (5 g, 6.96 mmol) in anhydrous DMF (100 mL) were added anhydrous K_2CO_3 (17.7 g, 128.11 mmol) and allyl bromide (10.07 g, 7.2 mL, 83.27 mmol). The resulting mixture was stirred until complete consumption of the starting material was achieved, as determined by TLC. The postreaction mixture was then diluted with AcOEt and washed with water (3×) and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness *in vacuo*. The product was isolated by flash column chromatography using 1% AcOEt/hexanes mixtures as the eluent to afford 7.1 g (94%) of compound allyl 2-(allyloxy)-4-fluorobenzoate as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.88−7.78 (m, 1H), 6.64−6.59 (m, 2H), 6.06−5.91 (m, 2H), 5.47 (dq, J 17.2, 1.6 Hz, 1H), 5.39−5.30 (m, 1H), 5.26 (dq, J 10.6, 1.4 Hz, 1H), 5.21 (dt, J 10.5, 1.3 Hz, 1H), 4.78−4.71 (m, 2H), 4.58−4.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.2, 164.9, and 162.5 (d, $J_{C\text{-}F}$ 241.9 Hz), 160.3 and 160.2 (d, $J_{C\text{-}F}$ 10.6 Hz), 133.9 and 133.8 (d, $J_{C\text{-}F}$ 10.9 Hz), 132.3, 132.0, 118.1, 117.9, 116.49, and 116.46 (d, $J_{C\text{-}F}$ 3.1 Hz), 107.4 and 107.2 (d, $J_{C\text{-}F}$ 21.7 Hz), 101.5 and 101.3 (d, $J_{C\text{-}F}$ 25.6 Hz), 69.7, 65.4; FTIR (film) ν: 3087, 2988, 2939, 2884, 1731, 1706, 1681, 1609, 1593, 1499, 1421, 1286, 1269, 1241, 1172, 1122, 1102, 1076, 1016, 997, 962, 932, 838, 770 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}O_3FNa$ [M + Na^+] 259.0746 found 259.0742.

Allyl 2-(Allyloxy)-4-chlorobenzoate. Prepared in the same manner as allyl 2-(allyloxy)-4-fluorobenzoate; yield 6.16 g (77%) starting from 5.4 g of 4-chlorosalicylic acid; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J 8.1 Hz, 1H), 7.00−6.93 (m, 2H), 6.10−5.95 (m, 2H), 5.51 (dq, J 17.3, 1.6 Hz, 1H), 5.40 (dq, J 17.2, 1.3 Hz, 1H), 5.31 (dq, J 10.6, 1.4 Hz, 1H), 5.26 (dq, J 10.6, 1.3 Hz, 1H), 4.79 (dt, J 5.6, 1.3 Hz, 2H), 4.60 (dt, J 4.9, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.0, 158.8, 139.2, 132.9, 132.1, 132.0, 120.6, 118.9, 118.2, 118.0, 114.1, 69.7, 65.6; FTIR (film) ν: 3085, 3020, 2986, 2937, 2877, 1731, 1594, 1487, 1410, 1281, 1243, 1133, 1074, 999, 930, 901, 771 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{13}O_3ClNa$ [M + Na^+] 275.0451; Found 275.0446.

Allyl 2-(Allyloxy)-6-methoxybenzoate. Prepared in the same manner as compound allyl 2-(allyloxy)-4-fluorobenzoate; yield 6.85 g (93%) starting from 5 g of 6-methoxysalicylic acid; yellowish oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.24 (t, J 8.4 Hz, 1H), 6.56−6.52 (m, 2H), 6.05−5.92 (m, 2H), 5.44−5.33 (m, 2H), 5.26−5.20 (m, 2H), 4.82 (dt, J 5.6, 1.5 Hz, 2H), 4.54 (dt, J 5.0, 1.7 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 157.4, 156.4, 132.8, 132.2, 130.9, 118.0, 117.2, 113.6, 105.4, 104.1, 69.4, 65.7, 56.0; FTIR (film) ν: 33085, 3015, 2981, 2940, 2842, 1732, 1597, 1472, 1424, 1297, 1255,. 1106, 1071, 929, 785, 730 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{16}O_4Na$ [M + Na^+] 271.0946; Found 271.0946.

(2-(Allyloxy)-4-fluorophenyl)methanol. To a solution of allyl 2-(allyloxy)-4-fluorobenzoate (7.0 g, 29.63 mmol) in dry THF (100 mL) cooled to −10 °C was added a 2 M soln. of $LiAlH_4$ in THF (35.56 mmol, 17.8 mL). After stirring for 30 min at −10 °C, the reaction mixture was adjusted to rt and stirred at the same temperature until complete consumption of the starting material was achieved, as determined by TLC (ca. 2−3 h). Then, the reaction mixture was poured into 2 M aq. NaOH and extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness *in vacuo*. The crude product was isolated by flash column chromatography on silica gel (10% AcOEt/hexanes) to afford 3.73 g (69%) of (2-(allyloxy)-4-fluorophenyl)methanol as a white solid; mp 53−54 °C ^1H NMR (400 MHz, $CDCl_3$) δ: 7.28−7.18 (m, 1H), 6.68−6.57 (m, 2H), 6.10−5.97 (m, 1H), 5.41 (dq, J 17.3, 1.5 Hz, 1H), 5.31 (dq, J 10.5, 1.9 Hz, 1H), 4.65 (s, 2H), 4.59−4.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.3 and 161.9 (d, $J_{C\text{-}F}$ 245.2 Hz), 157.4 and 157.3 (d, $J_{C\text{-}F}$ 10.2 Hz), 132.4, 129.6, and 129.5 (d, $J_{C\text{-}F}$ 10.1 Hz), 125.25 and 125.23 (d, $J_{C\text{-}F}$ 3.3 Hz), 118.0, 107.0, and 106.8 (d, $J_{C\text{-}F}$ 21.1 Hz), 100.1 and 99.9 (d, $J_{C\text{-}F}$ 26.0 Hz), 69.0, 61.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.0; FTIR (film) ν: 3361, 3085, 2926, 2874, 1610, 1503, 1421, 1277, 1152, 1012, 833 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{11}O_2F$ [M] 182.0743; Found 182.0746.

(2-(Allyloxy)-4-chlorophenyl)methanol. Prepared in the same manner as compound (2-(allyloxy)-4-fluorophenyl)methanol; yield 3.17 g (66%) starting from 6.1 g of allyl 2-(allyloxy)-4-chlorobenzoate; white solid, mp 50−51 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, J 8.0 Hz, 1H), 6.90 (dd, J 8.0, 1.9 Hz, 1H), 6.82 (d, J 1.9 Hz, 1H), 6.01 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.39 (dq, J 17.3, 1.6 Hz, 1H), 5.30 (dq, J 10.5, 1.4 Hz, 1H), 4.62 (s, 2H), 4.52 (dt, J 5.2, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 133.8, 132.4, 129.2, 128.1, 120.7, 118.0, 112.1, 69.0, 60.8; FTIR (film) ν: 3352, 3083, 2924, 2871, 1598, 1490, 1507, 1243, 1227, 1040, 1019, 1001, 926, 896, 837, 820 cm^{-1}; HRMS (EI) m/z calcd for $C_{10}H_{11}ClO_2$ [M] 198.0448; Found 198.0450.

(2-(Allyloxy)-6-methoxyphenyl)methanol. Prepared in the same manner as compound (2-(allyloxy)-4-fluorophenyl)methanol; yield 3.77 g (71%) starting from 6.8 g of allyl 2-(allyloxy)-6-methoxybenzoate; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19 (t, J 8.4 Hz, 1H), 6.56 (d, J 8.3 Hz, 1H), 6.55 (d, J 8.4 Hz, 1H), 6.06 (ddt, J 17.3, 10.4, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.7 Hz, 1H), 5.28 (dq, J 10.5, 1.4 Hz, 1H), 4.82 (d, J 6.8 Hz, 2H), 4.57 (dt, J 5.2, 1.5 Hz, 2H), 3.85 (s, 3H), 2.51 (t, J 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.5, 157.4, 133.2, 129.0, 117.6, 117.4, 105.2, 104.0, 69.3, 55.7, 54.9; FTIR (film) ν: 3578, 3452, 2999, 2938, 2888, 2839, 1596, 1474, 1259, 1198, 1105, 1003, 776, 737 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{11}H_{14}O_3Na$ [M + Na^+] 217.0841; Found 217.0839.

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2-(Allyloxy)-4-fluorobenzaldehyde (18g). A solution of alcohol (2-(allyloxy)-4-fluorophenyl)methanol (2.5 g, 13.72 mmol) in dry CH_2Cl_2 (10 mL) was added to a suspension of PCC (6.04 g, 27.44 mmol) in dry CH_2Cl_2 (40 mL). The reaction mixture was stirred at room temperature until complete consumption of the starting material was achieved, as determined by TLC (ca. 1.5 h). Then, the reaction mixture was diluted with Et_2O, Celite was added, and the resulting slurry was stirred for 30 min. Next, the solids were filtered off and the solution was concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% AcOEt/hexanes) to afford 2.17 g (87%) of aldehyde **18g** as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.40 (s, 1H), 7.85 (dd, *J* 8.6, 6.9 Hz, 1H), 6.74−6.69 (m, 1H), 6.66 (dd, *J* 10.8, 2.3 Hz, 1H), 6.05 (ddt, *J* 17.3, 10.5, 5.2 Hz, 1H), 5.45 (dq, *J* 17.3, 1.5 Hz, 1H), 5.38−5.33 (m, 1H), 4.63 (dt, *J* 5.2, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.1, 168.8, and 166.3 (d, $J_{C\text{-}F}$ 256.0 Hz), 162.6 and 162.5 (d, $J_{C\text{-}F}$ 11.0 Hz), 131.7, 130.8, and 130.7 (d, $J_{C\text{-}F}$ 11.6 Hz), 121.92 and 121.89 (d, $J_{C\text{-}F}$ 2.8 Hz), 118.6, 108.4, and 108.2 (d, $J_{C\text{-}F}$ 22.2 Hz), 100.9 and 100.6 (d, $J_{C\text{-}F}$ 25.8 Hz), 69.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −99.7; FTIR (film) *v*: 3113, 3079, 2991, 2918, 2873, 1680, 1607, 1590, 1277, 930 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_9FO_2$ [M] 180.0587; Found 180.0593.

2-(Allyloxy)-4-chlorobenzaldehyde (18f). Prepared in the same manner as compound **18g**; yield 2.45 g (82%) starting from 3.00 g of allyl 2-(allyloxy)-4-chlorobenzoate; white solid, mp 47−49 °C (Lit.[33b] 48−49 °C); spectral data in accordance with literature data:[33b] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.44 (d, *J* 0.8 Hz, 1H), 7.78−7.75 (m, 1H), 7.02−6.96 (m, 2H), 6.11−6.00 (m, 1H), 5.49−5.42 (m, 1H), 5.36 (dt, *J* 10.6, 1.3 Hz, 1H), 4.67−4.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 188.4, 161.2, 141.8, 131.7, 129.5, 123.6, 121.4, 118.6, 113.5, 69.5; FTIR (film) *v*: 3092, 3068, 2933, 2882, 1681, 1591, 1573, 1485, 1415, 1400, 1241, 997, 943, 812, 692, 453 cm^{-1}; LRMS (ESI-TOF) *m*/*z* 219 [M + Na$^+$].

2-(Allyloxy)-6-methoxybenzaldehyde (18k). Prepared in the same manner as compound **18g**; yield 3.28 g (88%) starting from 3.75 g of allyl 2-(allyloxy)-6-methoxybenzoate; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.52 (br s, 1H), 7.42−7.36 (m, 1H), 6.55 (d, *J* 8.2 Hz, 1H), 6.53 (d, *J* 8.4 Hz, 1H), 6.07−5.96 (m, 1H), 5.49−5.42 (m, 1H), 5.28 (dq, *J* 10.6, 1.1 Hz, 1H), 4.61−4.57 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.2, 161.8, 161.4, 135.7, 132.4, 117.7, 114.7, 105.1, 104.1, 69.4, 56.0; MS (ESI-TOF) *m*/*z* 215 [M + Na$^+$].

Olefination of 2-Allyloxybenzaldehydes. General Procedure. Neat triethyl phosphonoacetate (10 mmol) was added to a suspension of NaH (10 mmol) in dry THF (50 mL). After 30 min, a solution of salicylaldehyde derivative (8 mmol) in dry THF (10 mL) was added, and the resulting mixture was stirred overnight. The progress of the reaction was followed by TLC. The reaction was quenched by the addition of water (50 mL). The organic layer was separated, and the aqueous one was extracted with ether (3 × 50 mL). The combined organic solutions were dried over anhydrous Na_2SO_4, the volatiles were removed under reduced pressure, and the residue was purified by column chromatography.

Ethyl (*E*)-3-(2-(Allyloxy)phenyl)acrylate (19a). Yield 18.2 g (82%) starting from 15.57 g of compound **18a**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (d, *J* 16.2 Hz, 1H), 7.50 (dd, *J* 7.7, 1.7 Hz, 1H), 7.32−7.26 (m, 1H), 6.96−6.91 (m, 2H), 6.87 (d, *J* 8.3 Hz, 1H), 6.52 (d, *J* 16.2 Hz, 1H), 6.06 (ddt, *J* 17.3, 10.3, 5.1 Hz, 1H), 5.41 (dq, *J* 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* 10.6, 1.3 Hz, 1H), 4.61−4.57 (m, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.4, 157.3, 139.9, 132.9, 131.3, 128.7, 123.7, 120.9, 118.8, 117.6, 112.5, 69.1, 60.3, 14.3; FTIR (film) *v*: 2981, 2936, 2903, 2871, 1710, 1631, 1598, 1488, 1454, 1366, 1318, 1270, 1270, 1243, 1175, 1037, 991, 753 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{16}O_3Na$ [M + Na$^+$] 255.0997; Found 255.0994.

Ethyl (*E*)-3-(2-(Allyloxy)-5-methylphenyl)acrylate (19b). Yield 8.02 g (91%) starting from 6.29 g of salicylaldehyde **18b**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* 16.2 Hz, 1H), 7.35−7.27 (m, 1H), 7.08 (d, *J* 8.4 Hz, 1H), 6.77 (d, *J* 8.4 Hz, 1H), 6.50 (d, *J* 16.2 Hz, 1H), 6.12−5.96 (m, 1H), 5.40 (dt, *J* 17.3, 1.6 Hz, 1H), 5.32−5.22 (m, 1H), 4.58−4.51 (m, 2H), 4.24 (q, *J* 7.1 Hz, 2H), 2.27 (s, 3H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.4, 155.3, 140.0, 133.1, 131.8, 130.0, 129.1, 123.4, 118.5, 117.5, 112.6, 69.3, 60.2, 20.4, 14.3; FTIR (film) v: 3080, 3020, 2981, 2925, 2869, 1710, 1631, 1495, 1319, 1272, 1244, 1175, 1165, 1038, 991, 807 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{18}O_3Na$ [M + Na$^+$] 269.1154; Found 269.1154.

Ethyl (*E*)-3-(2-(Allyloxy)-4-methylphenyl)acrylate (19c). Yield 8.61 g (93%) starting from 6.65 g of salicylaldehyde **18c**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (d, *J* 16.2 Hz, 1H), 7.38 (d, *J* 7.8 Hz, 1H), 6.81−6.71 (m, 1H), 6.69 (s, 1H), 6.47 (d, *J* 16.1 Hz, 1H), 6.06 (ddt, *J* 17.3, 10.4, 5.1 Hz, 1H), 5.41 (dq, *J* 17.3, 1.7 Hz, 1H), 5.29 (dq, *J* 10.6, 1.4 Hz, 1H), 4.57 (dt, *J* 5.1, 1.5 Hz, 2H), 4.24 (q, *J* 7.1 Hz, 2H), 2.33 (s, 3H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.6, 157.3, 142.0, 139.9, 133.0, 128.7, 121.7, 121.0, 117.6, 117.5, 113.3, 69.1, 60.1, 21.8, 14.3; FTIR (film) *v*: 3981, 2926, 2870, 1710, 1630, 1609, 1317, 1269, 1175, 1031, 990, 809 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{18}O_3Na$ [M + Na$^+$] 269.1154; Found 269.1155.

Ethyl (*E*)-3-(2-(Allyloxy)-3-methylphenyl)acrylate (19d). Yield 7.90 g (92%) starting from 6.16 g of salicylaldehyde **18d**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* 16.2 Hz, 1H), 7.42−7.37 (m, 1H), 7.22−7.18 (m, 1H), 7.02 (t, *J* 7.6 Hz, 1H), 6.45 (d, *J* 16.2 Hz, 1H), 6.10 (ddt, *J* 17.1, 10.4, 5.6 Hz, 1H), 5.43 (dq, *J* 17.1, 1.6 Hz, 1H), 5.28 (dq, *J* 10.4, 1.2 Hz, 1H), 4.32 (dt, *J* 5.6, 1.4 Hz, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 2.29 (s, 3H), 1.33 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.1, 156.6, 139.9, 133.3, 133.1, 132.0, 128.2, 125.4, 124.2, 119.1, 117.9, 74.9, 60.3, 21.0, 16.2, 14.3; FTIR (film) *v*: 3069, 2981, 2929, 2865, 1713, 1623, 1465, 1314, 1267, 1249, 1197, 1177, 1165, 988, 787 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{18}O_3Na$ [M + Na$^+$] 269.1154; Found 269.1144.

Ethyl (*E*)-3-(2-(Allyloxy)-5-chlorophenyl)acrylate (19e). Yield 7.98 g (95%) starting from 6.17 g of salicylaldehyde **18e**; colorless crystals; mp 49−50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* 16.2 Hz, 1H), 7.47 (d, *J* 2.6 Hz, 1H), 7.24 (dd, *J* 8.8, 2.6 Hz, 1H), 6.82 (d, *J* 8.9 Hz, 1H), 6.48 (d, *J* 16.2 Hz, 1H), 6.04 (ddt, *J* 17.3, 10.5, 5.2 Hz, 1H), 5.40 (dq, *J* 17.3, 1.6 Hz, 1H), 5.31 (dq, *J* 10.6, 1.4 Hz, 1H), 4.59 (dt, *J* 5.2, 1.5 Hz, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 1.33 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.0, 155.7, 138.4, 132.5, 130.7, 128.1, 126.0, 125.3, 120.0, 118.0, 113.9, 69.5, 60.5, 14.3; FTIR (film) *v*: 2982, 2936, 1711, 1633, 1483, 1316, 1269, 1252, 1177, 986 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{15}O_3ClNa$ [M + Na$^+$] 289.0607; Found 289.0600.

Ethyl (*E*)-3-(2-(Allyloxy)-4-chlorophenyl)acrylate (19f). Yield 2.82 g (85%) starting from 2.45 g of aldehyde **18f**; colorless oil; spectral data in accordance with the literature:[33b] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, *J* 16.2 Hz, 1H), 7.42 (d, *J* 8.3 Hz, 1H), 6.93 (dd, *J* 8.3, 2.0 Hz, 1H), 6.88 (d, *J* 2.0 Hz, 1H), 6.48 (d, *J* 16.2 Hz, 1H), 6.05 (ddt, *J* 17.3, 10.5, 5.2 Hz, 1H), 5.43 (dq, *J* 17.3, 1.5 Hz, 1H), 5.33 (dq, *J* 10.5, 1.3 Hz, 1H), 4.60 (dt, *J* 5.2, 1.5 Hz, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.2, 157.6, 138.7, 136.7, 132.2, 129.5, 122.4, 121.1, 119.2, 118.2, 113.1, 69.5, 60.4, 14.3; FTIR (film) v: 3078, 2981, 2937, 2902, 2872, 1709, 1631, 1591, 1487, 1412, 1314, 1247, 1174, 987, 901, 807 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{15}O_3ClNa$ [M + Na$^+$] 289.0607; Found 289.0606.

Ethyl (*E*)-3-(2-(Allyloxy)-4-fluorophenyl)acrylate (19g). Yield 2.40 g (81%) starting from 2.13 g of salicylaldehyde **18g**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, *J* 16.2 Hz, 1H), 7.47 (dd, *J* 8.6, 6.7 Hz, 1H), 6.65 (td, *J* 8.2, 2.4 Hz, 1H), 6.61 (dd, *J* 10.8, 2.4 Hz, 1H), 6.45 (d, *J* 16.2 Hz, 1H), 6.05 (ddt, *J* 17.3, 10.5, 5.2 Hz, 1H), 5.42 (dq, *J* 17.3, 1.7 Hz, 1H), 5.32 (dq, *J* 10.5, 1.4 Hz, 1H), 4.58 (dt, *J* 5.2, 1.5 Hz, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.3, 165.9, and 163.4 (d, $J_{C\text{-}F}$ 250.6 Hz), 158.6 and 158.5 (d, $J_{C\text{-}F}$ 10.1 Hz), 138.9, 132.2, 130.1, and 130.0 (d, $J_{C\text{-}F}$ 10.5 Hz), 120.03 and 120.00 (d, $J_{C\text{-}F}$ 3.3 Hz), 118.28, 118.25, 118.22, 107.9, and 107.7 (d, $J_{C\text{-}F}$ 21.9 Hz), 100.7 and 100.5 (d, $J_{C\text{-}F}$ 25.8 Hz), 69.5, 60.3, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.2; FTIR (film) *v*: 3084, 2983, 2937, 2903, 1710, 1632, 1605, 1590, 1499, 1421, 1320, 1284, 1262, 1176, 1021, 987, 835 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{15}O_3FNa$ [M + Na$^+$] 273.0903; Found 273.0899.

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Ethyl (*E*)-3-(2-(Allyloxy)-5-methoxyphenyl)acrylate (19h). Yield 7.41 g (91%) starting from 5.96 g of salicylaldehyde **18h**; yellowish oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.88 (d, J 16.2 Hz, 1H), 7.26 (d, J 3.0 Hz, 1H), 7.00 (d, J 9.0 Hz, 1H), 6.95 (dd, J 9.0, 3.0 Hz, 1H), 6.65 (d, J 16.2 Hz, 1H), 6.04 (ddt, J 17.2, 10.4, 5.2 Hz, 1H), 5.38 (dq, J 17.2, 1.7 Hz, 1H), 5.26 (dq, J 10.5, 1.5 Hz, 1H), 4.60−4.56 (m, 2H), 4.16 (q, J 7.1 Hz, 2H), 3.73 (s, 3H), 1.23 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 166.9, 153.8, 151.5, 139.3, 134.1, 123.7, 119.0, 118.3, 117.9, 115.0, 113.0, 69.8, 60.4, 56.0, 14.6; FTIR (film) ν: 3079, 2982, 2938, 2907, 2835, 1710, 1631, 1495, 1288, 1259, 1216, 1175, 1042, 990 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{18}O_4Na$ [M + Na$^+$] 285.1103; Found 285.1100.

Ethyl (*E*)-3-(2-(Allyloxy)-4-methoxyphenyl)acrylate (19i). Yield 8.70 g (96%) starting from 6.59 g of salicylaldehyde **18i**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (d, J 16.1 Hz, 1H), 7.43 (d, J 8.6 Hz, 1H), 6.48 (dd, J 8.6, 2.4 Hz, 1H), 6.43−6.38 (m, 2H), 6.06 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.30 (dq, J 10.5, 1.4 Hz, 1H), 4.57 (dt, J 5.2, 1.5 Hz, 2H), 4.23 (q, J 7.1 Hz, 2H), 3.79 (s, 3H), 1.31 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.8, 162.5, 158.7, 139.8, 132.7, 130.1, 117.8, 116.9, 116.1, 105.6, 99.6, 69.2, 60.1, 55.4, 14.4; FTIR (film) ν: 3082, 2980, 2937, 2839, 1706, 1606, 1302, 1261, 1202, 1166, 1039, 832 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{18}O_4Na$ [M + Na$^+$] 285.1103, Found 285.1096.

Ethyl (*E*)-3-(2-(Allyloxy)-3-methoxyphenyl)acrylate (19j). Yield 5.92 g (83%) starting from 5.2 g of salicylaldehyde **18i**; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, J 16.2 Hz, 1H), 7.14−7.10 (m, 1H), 7.01 (t, J 8.0 Hz, 1H), 6.92−6.87 (m, 1H), 6.44 (d, J 16.2 Hz, 1H), 6.13−6.01 (m, 1H), 5.34 (dq, J 17.2, 1.5 Hz, 1H), 5.21 (dq, J 10.4, 1.9 Hz, 1H), 4.50 (dt, J 6.0, 1.1 Hz, 2H), 4.23 (q, J 7.1 Hz, 2H), 3.83 (s, 3H), 1.30 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.0, 153.1, 147.1, 139.6, 133.8, 129.0, 124.1, 119.4, 119.0, 118.0, 113.9, 74.5, 60.3, 55.8, 14.3; FTIR (film) ν: 3078, 2980, 2938, 2839, 1712, 1634, 1578, 1478, 1269, 1182, 987, 790 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{18}O_4Na$ [M + Na$^+$] 285.1103; Found 285.1096.

Ethyl (*E*)-3-(2-(Allyloxy)-6-methoxyphenyl)acrylate (19k). Yield 3.8 g (85%) starting from 3.28 g of salicylaldehyde **18k**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J 16.3 Hz, 1H), 7.22 (t, J 8.4 Hz, 1H), 6.89 (d, J 16.3 Hz, 1H), 6.55 (d, J 8.4 Hz, 1H), 6.54 (d, J 8.4 Hz, 1H), 6.07 (ddt, J 17.3, 10.6, 5.1 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.29 (dq, J 10.6, 1.3 Hz, 1H), 4.61 (dt, J 5.1, 1.5 Hz, 2H), 4.25 (q, J 7.1 Hz, 2H), 3.87 (s, 3H), 1.33 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.5, 160.1, 158.9, 135.4, 132.9, 130.9, 120.9, 117.6, 112.7, 105.0, 103.8, 69.4, 60.1, 55.7, 14.4; FTIR (film) ν: 2980, 2939, 2902, 2871, 1707, 1624, 1593, 1578, 1474, 1309, 1256, 1164, 1104, 966, 743 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{18}O_4Na$ [M + Na$^+$] 285.1103; Found 285.1105.

Ethyl (*E*)-3-(2-(Allyloxy)-5-nitrophenyl)acrylate (19l). Yield 6.43 g (78%) starting from 6.12 g of salicylaldehyde **18l**; yellowish solid, mp 62−64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, J 2.8 Hz, 1H), 8.20 (dd, J 9.1, 2.8 Hz, 1H), 7.96 (d, J 16.2 Hz, 1H), 6.97 (d, J 9.1 Hz, 1H), 6.60 (d, J 16.2 Hz, 1H), 6.06 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.44 (dq, J 17.3, 1.6 Hz, 1H), 5.38 (dt, J 10.5, 1.3 Hz, 1H), 4.74 (dt, J 5.2, 1.5 Hz, 2H), 4.28 (q, J 7.1 Hz, 2H), 1.34 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 161.4, 141.5, 137.3, 131.5, 126.5, 124.5, 124.1, 121.6, 119.0, 112.2, 70.0, 60.7, 14.3; FTIR (film) ν: 3086, 2983, 2937, 2904, 1712, 1519, 1343, 1276, 989, 742 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{15}NO_5Na$ [M + Na$^+$] 300.0848; Found 300.0835.

Ethyl (*E*)-3-(2-(Allyloxy)-6-methoxy-4-nitrophenyl)acrylate (19m). Yield 7.05 g (92%) starting from 5.90 g of aldehyde **18m**; yellow solid, mp 85−86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, J 16.1 Hz, 1H), 7.34 (d, J 3.1 Hz, 1H), 7.28 (d, J 3.1 Hz, 1H), 6.48 (d, J 16.1 Hz, 1H), 6.06 (ddt, J 17.4, 10.4, 6.0 Hz, 1H), 5.39 (dq, J 17.4, 1.4 Hz, 1H), 5.31 (d, J 10.4 Hz, 1H), 4.47 (d, J 6.0 Hz, 2H), 4.28 (q, J 7.1 Hz, 2H), 3.85 (s, 3H), 1.34 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 155.3, 145.1, 144.5, 137.3, 132.2, 132.1, 122.1, 119.6, 117.5, 111.1, 77.4, 60.8, 56.1, 14.2; FTIR (film) ν: 3095, 2985, 2942, 2910, 1718, 1639, 1529, 1429, 1319, 1639, 1529, 1429, 1319, 1218, 1187, 1039, 985, 973, 938, 863, 741 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}NO_6Na$ [M + Na$^+$] 330.0954; Found 330.0951.

Ethyl (*E*)-3-(2-(Allyloxy)naphthalen-1-yl)acrylate (19n). Yield 4.34 g (91%) starting from 3.57 g of aldehyde **18n**; yellowish solid, mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, J 16.2 Hz, 1H), 8.21−8.17 (m, 1H), 7.81 (d, J 9.1 Hz, 1H), 7.79−7.77 (m, 1H), 7.52 (ddd, J 8.5, 6.8, 1.4 Hz, 1H), 7.38 (ddd, J 8.0, 6.8, 1.0 Hz, 1H), 7.25 (d, J 9.1 Hz, 1H), 6.77 (d, J 16.2 Hz, 1H), 6.10 (ddt, J 17.3, 10.4, 5.1 Hz, 1H), 5.45 (dq, J 17.3, 1.7 Hz, 1H), 5.32 (dq, J 10.6, 1.4 Hz, 1H), 4.75 (dt, J 5.1, 1.6 Hz, 2H), 4.33 (q, J 7.1 Hz, 2H), 1.38 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.8, 155.6, 137.7, 133.0, 132.7, 131.3, 129.1, 128.5, 127.3, 124.0, 123.7, 123.4, 117.8, 117.4, 114.3, 70.0, 60.4, 14.4; FTIR (film) ν: 3072, 2981, 2935, 1708, 1625, 1591, 1512, 1466, 1367, 1284, 1266, 1174, 1161, 1042, 807, 747 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}O_3Na$ [M + Na$^+$] 305.1154; Found 305.1152.

Synthesis of Allyl Alcohols 20. General Procedure. To a cooled (−70 °C) solution of the unsaturated ester (8 mmol) in CH_2Cl_2 (50 mL) was added a 1 M soln. of DIBAL-H in hexanes (20 mL, 20 mmol). The progress of the reduction was followed by TLC. When the reduction was complete, the reaction was quenched by the addition of sat. aq. Na_2SO_4 (4.4 mL). When a precipitate appeared, the mixture was diluted with Et_2O and stirred for 1 h. Solids were filtered off and washed with Et_2O. After drying over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crude alcohol was purified by flash column chromatography.

(*E*)-3-(2-(Allyloxy)phenyl)prop-2-en-1-ol (20a). Yield 14.1 g (94%) starting from ester **19a**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J 7.7, 1.7 Hz, 1H), 7.19 (ddd, J 8.3, 7.5, 1.7 Hz, 1H), 6.97 (d, J 16.0 Hz, 1H), 6.95−6.89 (m, 1H), 6.85 (d, J 8.3 Hz, 1H), 6.38 (dt, J 16.0, 5.9 Hz, 1H), 6.07 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.28 (dq, J 10.5, 1.4 Hz, 1H), 4.55 (dt, J 5.2, 1.5 Hz, 2H), 4.30 (dd, J 5.9, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.7, 133.4, 129.4, 128.6, 127.0, 126.2, 125.9, 120.9, 117.4, 112.4, 69.2, 64.0; FTIR (film) ν: 3346, 3074, 3033, 2919, 2865, 1597, 1488, 1451, 1240, 1223, 1017, 998, 975, 751 cm^{-1}; HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ [M] 190.0994; Found 190.0991.

(*E*)-3-(2-(Allyloxy)-5-methylphenyl)prop-2-en-1-ol (20b). Yield 5.54 g (83%) starting from 8.02 g of ester **19b**; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (d, J 2.1 Hz, 1H), 7.00 (dd, J 8.4, 1.9 Hz, 1H), 6.97−6.88 (m, 1H), 6.76 (d, J 8.3 Hz, 1H), 6.37 (dt, J 16.0, 5.9 Hz, 1H), 6.07 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.7 Hz, 1H), 5.27 (dq, J 10.5, 1.4 Hz, 1H), 4.53 (dt, J 5.2, 1.5 Hz, 2H), 4.30 (dd, J 5.9, 1.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.6, 133.4, 129.9, 129.0, 128.9, 127.4, 126.0, 125.7, 117.2, 112.4, 69.3, 64.0, 20.4; FTIR (film) v: 3347, 3082, 3021, 2921, 2862, 1495, 1455, 1423, 1244, 1120, 1090, 1020, 998, 973, 929, 805 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}O_2Na$ [M + Na$^+$] 227.1048; Found 227.1048.

(*E*)-3-(2-(Allyloxy)-4-methylphenyl)prop-2-en-1-ol (20c). Yield 5.79 g (81%) starting from 8.61 g of ester **19c**; white solid, mp 61−62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (d, J 7.8 Hz, 1H), 6.93 (d, J 16.0 Hz, 1H), 6.75 (d, J 7.8 Hz, 1H), 6.68 (s, 1H), 6.36 (dt, J 16.0, 6.0 Hz, 1H), 6.08 (ddt, J 17.1, 10.4, 5.2 Hz, 1H), 5.42 (dq, J 17.3, 1.4 Hz, 2H), 5.32−5.26 (m, 2H), 4.58−4.53 (m, 2H), 4.31 (t, J 4.6 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.7, 138.9, 133.4, 128.1, 126.8, 126.3, 123.1, 121.6, 117.4, 113.2, 69.1, 64.4, 21.6; FTIR (film) ν: 3344, 3288, 3096, 3040, 2992, 2939, 2915, 2859, 1609, 1417, 1264, 1170, 1121, 1028, 976, 917, 812 cm^{-1}; HRMS (ESI-TOF) m/z $C_{13}H_{16}O_2Na$ [M + Na$^+$] 227.1048; Found 227.1048.

(*E*)-3-(2-(Allyloxy)-3-methylphenyl)prop-2-en-1-ol (20d). Yield 5.56 g (85%) starting from 7.93 g of ester **19d**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (dd, J 7.7, 1.3 Hz, 1H), 7.10−7.06 (m, 1H), 6.98 (t, J 7.6 Hz, 1H), 6.88 (d, J 16.0 Hz, 1H), 6.36 (dt, J 16.0, 5.8 Hz, 1H), 6.10 (ddt, J 17.1, 10.7, 5.5 Hz, 1H), 5.43 (dq, J 17.2, 1.6 Hz, 1H), 5.26 (dq, J 10.4, 1.3 Hz, 1H), 4.32−4.29 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.0, 133.8, 131.5, 130.5, 130.2, 129.7, 126.1, 124.4, 124.1, 117.3, 74.1, 64.0, 16.2; FTIR (film) ν: 3344, 3068, 3016, 2920, 2861, 1461, 1420, 1254, 1191, 1089,

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987, 928, 773 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}O_2Na$ [M + Na^+] 227.1048; Found 227.1038.

(*E*)-3-(2-(Allyloxy)-5-chlorophenyl)prop-2-en-1-ol (20e). Yield 5.77 g (96%) starting from 7.97 g of ester **19e**; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J 2.6 Hz, 1H), 7.13 (dd, J 8.8, 2.6 Hz, 1H), 6.88 (dt, J 16.0, 1.5 Hz, 1H), 6.77 (d, J 8.8 Hz, 1H), 6.37 (dt, J 16.0, 5.7 Hz, 1H), 6.04 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.39 (dq, J 17.3, 1.6 Hz, 1H), 5.29 (dq, J 10.5, 1.4 Hz, 1H), 4.53 (dt, J 5.2, 1.5 Hz, 2H), 4.35−4.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 154.2, 132.9, 130.5, 128.1, 127.7, 126.7, 125.9, 124.7, 117.8, 113.6, 69.5, 63.9; FTIR (film) ν: 3399, 2918, 2866, 1483, 1244, 1130, 1016, 997, 927, 805 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}O_2ClNa$ [M + Na^+] 247.0502; Found 247.0496.

(*E*)-3-(2-(Allyloxy)-4-chlorophenyl)prop-2-en-1-ol (20f). Yield 1.65 g (69%) starting from 2.82 g of ester **19f**; white solid, mp 53−54 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J 8.2 Hz, 1H), 6.92−6.82 (m, 3H), 6.36 (dt, J 16.0, 5.8 Hz, 1H), 6.05 (ddt, J 17.2, 10.5, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.5 Hz, 1H), 5.31 (dq, J 10.5, 1.3 Hz, 1H), 4.54 (dt, J 5.2, 1.5 Hz, 2H), 4.31 (br d, J 5.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 133.8, 132.6, 129.6, 127.7, 125.1, 124.6, 121.0, 117.9, 112.9, 69.4, 64.1; MS (ESI-TOF) m/z 247 [M + Na^+].

(*E*)-3-(2-(Allyloxy)-4-fluorophenyl)prop-2-en-1-ol (20g). Yield 1.31 g (65%) starting from 2.40 g of ester **19g**; white solid, mp 46−47 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.39−7.32 (m, 1H), 6.85 (d, J 16.0 Hz, 1H), 6.64−6.55 (m, 2H), 6.35−6.25 (m, 1H), 6.09−5.98 (m, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.30 (dq, J 10.6, 1.4 Hz, 1H), 4.52 (dq, J 5.0, 1.5 Hz, 2H), 4.29 (d, J 5.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.2 and 161.8 (d, $J_{C\text{-}F}$ 246.4 Hz), 156.7 and 156.6 (d, $J_{C\text{-}F}$ 9.8 Hz), 132.6, 128.78, and 128.76 (d, $J_{C\text{-}F}$ 2.1 Hz), 127.9, 127.8, 125.3, 122.14, and 122.11 (d, $J_{C\text{-}F}$ 3.4 Hz), 117.9, 107.5, and 107.3 (d, $J_{C\text{-}F}$ 21.4 Hz), 100.4 and 100.2 (d, $J_{C\text{-}F}$ 25.6 Hz), 69.3, 64.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −111.7; FTIR (film) ν: 3347, 3084, 3044, 3018, 2987, 2924, 2867, 1604, 1498, 1420, 1278, 1164, 1019, 971, 835 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}O_2FNa$ [M + Na^+] 231.0797; Found 231.0795.

(*E*)-3-(2-(Allyloxy)-5-methoxyphenyl)prop-2-en-1-ol (20h). Yield 5.35 g (86%) starting from 7.41 g of ester **19h**; white solid, mp 41−42 °C [lit.[33b] 41−43 °C]; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.00 (d, J 3.0 Hz, 1H), 6.93 (dt, J 16.0, 1.3 Hz, 1H), 6.80 (d, J 8.9 Hz, 1H), 6.74 (dd, J 8.9, 3.0 Hz, 1H), 6.37 (dt, J 16.0, 5.9 Hz, 1H), 6.05 (ddt, J 17.2, 10.5, 5.2 Hz, 1H), 5.39 (dq, J 17.3, 1.6 Hz, 1H), 5.26 (dq, J 10.5, 1.4 Hz, 1H), 4.50 (dt, J 5.2, 1.5 Hz, 2H), 4.34−4.28 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.9, 150.2, 133.6, 129.5, 127.1, 126.0, 117.3, 114.1, 113.8, 112.1, 70.2, 64.1, 55.7; FTIR (film) ν: 3379, 3081, 3040, 2999, 2937, 2911, 2865, 2835, 1495, 1425, 1285,1214, 1043, 974 cm^{-1}; HRMS (EI) m/z calcd for $C_{13}H_{16}O_3$ [M] 220.1099; Found 220.1097.

(*E*)-3-(2-(Allyloxy)-4-methoxyphenyl)prop-2-en-1-ol (20i). Yield 4.23 g (58%) starting from 8.7 g of ester **19i**; white solid, mp 52−53 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J 8.5 Hz, 1H), 6.86 (dt, J 16.0, 1.4 Hz, 1H), 6.47 (dd, J 8.5, 2.4 Hz, 1H), 6.43 (d, J 2.4 Hz, 1H), 6.28 (dt, J 16.0, 6.1 Hz, 1H), 6.06 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.28 (dq, J 10.5, 1.4 Hz, 1H), 4.54 (dt, J 5.2, 1.5 Hz, 2H), 4.30−4.25 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.4, 156.8, 133.2, 127.7, 127.0, 126.2, 119.0, 117.5, 105.3, 99.7, 69.2, 64.4, 55.3; FTIR (film) ν: 3377, 2935, 2863, 1607, 1503, 1276, 1199, 1166, 1004, 973, 930, 833 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}O_3Na$ [M + Na^+] 243.0997; Found 243.0992.

(*E*)-3-(2-(Allyloxy)-3-methoxyphenyl)prop-2-en-1-ol (20j). Yield 3.68 g (78%) starting from 5.58 g of ester **19j**; yellowish oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.09 (dd, J 7.9, 1.4 Hz, 1H), 7.01 (t, J 8.0 Hz, 1H), 6.94 (d, J 16.1 Hz, 1H), 6.82 (dd, J 8.0, 1.5 Hz, 1H), 6.38 (dt, J 16.1, 5.9 Hz, 1H), 6.10 (ddt, J 17.2, 10.4, 5.9 Hz, 1H), 5.36 (dq, J 17.2, 1.6 Hz, 1H), 5.24−5.20 (m, 1H), 4.48 (dt, J 5.9, 1.3 Hz, 2H), 4.32 (dd, J 5.9, 1.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.0, 145.5, 134.2, 131.1, 129.8, 125.8, 124.0, 118.2, 117.5, 111.5, 74.1, 64.1, 55.8; FTIR (film) ν: 3390, 3078, 3010, 2937, 2864, 1577, 1475, 1462, 1440, 1270, 1207, 1090, 1067, 984, 930, 776, 746 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}O_3Na$ [M + Na^+] 243.0997; Found 243.0991.

(*E*)-3-(2-(Allyloxy)-6-methoxyphenyl)prop-2-en-1-ol (20k). Yield 2.1 g (67%) starting from 3.7 g of ester **19k**; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.12 (t, J 8.4 Hz, 1H), 6.91 (d, J 16.2 Hz, 1H), 6.81 (dt, J 16.2, 5.7 Hz, 1H), 6.55 (d, J 8.4 Hz, 1H), 6.54 (d, J 8.4 Hz, 1H), 6.07 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.27 (dq, J 10.6, 1.4 Hz, 1H), 4.57 (dt, J 5.2, 1.5 Hz, 2H), 4.32 (t, J 5.1 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.6, 157.5, 133.4, 132.7, 128.1, 121.9, 117.4, 114.3, 105.4, 104.0, 69.5, 65.5, 55.7; FTIR (film) ν: 3372, 3091, 3002, 2937, 2864, 2839, 1583, 1471, 1438, 1251, 1200, 1113, 1079, 981, 770, 718 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{16}O_3Na$ [M + Na^+] 243.0997; Found 243.0995.

(*E*)-3-(2-(Allyloxy)-5-nitrophenyl)prop-2-en-1-ol (20l). Yield 3.58 g (66%) starting from 6.43 g of ester **19l**; yellow solid, mp 61−62 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, J 2.8 Hz, 1H), 8.09 (dd, J 9.1, 2.8 Hz, 1H), 6.99−6.86 (m, 2H), 6.51 (dt, J 16.0, 5.4 Hz, 1H), 6.06 (ddt, J 17.2, 10.5, 5.2 Hz, 1H), 5.43 (dq, J 17.2, 1.6 Hz, 1H), 5.35 (dq, J 10.5, 1.3 Hz, 1H), 4.68 (dt, J 5.2, 1.4 Hz, 2H), 4.37 (td, J 5.7, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.2, 141.6, 132.2, 131.9, 127.0, 124.3, 123.6, 122.5, 118.6, 111.6, 69.7, 63.6; FTIR (film) ν: 3240, 3084, 3023, 2921, 2867, 1582, 1513, 1339, 1277, 1256, 1081, 993, 746 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{12}H_{13}NO_4Na$ [M + Na^+] 258.0742; Found 258.0736.

(*E*)-3-(2-(Allyloxy)-6-methoxy-4-nitrophenyl)prop-2-en-1-ol (20m). Yield 4.19 g (69%) starting from 7.05 g of ester **19m**; yellow solid, mp 62−63 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.19 (s, 1H), 6.84 (dt, J 16.0, 1.6 Hz, 1H), 6.41 (dt, J 16.0, 5.4 Hz, 1H), 6.04 (ddt, J 17.2, 10.4, 5.8 Hz, 1H), 5.36 (dq, J 17.2, 1.4 Hz, 1H), 5.26 (dd, J 10.4, 1.3 Hz, 1H), 4.43 (dt, J 5.8, 1.2 Hz, 2H), 4.38−4.28 (m, 2H), 3.82 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.2, 144.9, 143.2, 134.4, 132.8, 132.7, 123.6, 118.9, 117.1, 108.5, 76.4, 63.4, 56.0; FTIR (film) ν: 3245, 3097, 2942, 2842, 1530, 1352, 1210, 1055, 975, 932 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}NO_5Na$ [M + Na^+] 288.0848; Found 288.0840.

(*E*)-3-(2-(Allyloxy)naphthalen-1-yl)prop-2-en-1-ol (20n). Yield 2.96 g (80%) starting from 4.34 g of ester **19n**; white solid, mp 59−60 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.18−8.13 (m, 1H), 7.79−7.76 (m, 1H), 7.73 (d, J 9.0 Hz, 1H), 7.46 (ddd, J 8.5, 6.8, 1.4 Hz, 1H), 7.35 (ddd, J 8.0, 6.8, 1.1 Hz, 1H), 7.24 (d, J 9.1 Hz, 1H), 7.04 (dt, J 16.2, 1.6 Hz, 1H), 6.46 (dt, J 16.2, 5.7 Hz, 1H), 6.10 (ddt, J 17.2, 10.4, 5.1 Hz, 1H), 5.44 (dq, J 17.2, 1.7 Hz, 1H), 5.29 (dq, J 10.5, 1.5 Hz, 1H), 4.68 (dt, J 5.1, 1.6 Hz, 2H), 4.48−4.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.5, 135.1, 133.6, 132.6, 129.4, 128.7, 128.3, 126.4, 124.2, 124.0, 123.7, 120.6, 117.4, 114.9, 70.2, 64.5; FTIR (film) ν: 3344, 3068, 3053, 2919, 2864, 1591, 1509, 1263, 1243, 1221, 1092, 927, 806, 747 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{16}O_2Na$ [M + Na^+] 263.1048; Found 263.1048.

Synthesis of Allyl Carbamates 21. General Procedure. To a solution of allyl alcohol (8 mmol) in CH_2Cl_2 (50 mL) cooled to −10 °C was added TCAI (10.4 mmol). After 1 h, the solvent was removed under reduced pressure, the residue was dissolved in a mixture of MeOH/H_2O (50 mL, 4:1 v/v), and K_2CO_3 (4 g) was added in one portion. After 1.5 h, MeOH was removed under reduced pressure and the aqueous residue was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and filtered through a silica gel pad, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel to afford the corresponding allyl carbamate **21**.

(*E*)-3-(2-(Allyloxy)phenyl)allyl Carbamate (21a). Yield 4.88 g (85%) starting from 4.68 g of allyl alcohol **20a**; white solid; mp 65−66 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.45 (dd, J 7.6, 1.5 Hz, 1H), 7.23−7.19 (m, 1H), 7.02 (d, J 16.0 Hz, 1H), 6.93 (t, J 7.5 Hz, 1H), 6.86 (d, J 8.2 Hz, 1H), 6.32 (dt, J 16.0, 6.5 Hz, 1H), 6.08 (ddt, J 17.2, 10.4, 5.2 Hz, 1H), 5.42 (dq, J 17.2, 1.6 Hz, 1H), 5.29 (dq, J 10.6, 1.4 Hz, 1H), 4.78 (s, 2H), 4.74 (dd, J 6.5, 1.3 Hz, 2H), 4.57 (dt, J 5.1, 1.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.9, 156.0, 133.4, 129.1, 129.0, 127.3, 125.7, 124.2, 121.0, 117.6, 112.5, 69.3, 66.4; FTIR (film) ν: 3431, 3336, 3270, 3213, 2925, 2868, 1687, 1613, 1489, 1451, 1422,

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1346, 1244, 1050, 973, 749 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{15}NO_3Na$ [M + Na^+] 256.0950; Found 256.0946.

(*E*)-3-(2-(Allyloxy)-5-methylphenyl)allyl Carbamate (21b). Yield 6.11 g (91%) starting from 5.54 g of allyl alcohol **20b**; white solid; mp 79−80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (s, 1H), 7.03−6.94 (m, 2H), 6.75 (d, J 8.4 Hz, 1H), 6.31 (dt, J 16.0, 6.5 Hz, 1H), 6.06 (ddt, J 17.3, 10.4, 5.2 Hz, 1H), 5.40 (dq, J 17.3, 1.7 Hz, 1H), 5.27 (dq, J 10.5, 1.5 Hz, 1H), 4.83 (br s, 2H), 4.73 (dd, J 6.5, 1.4 Hz, 1H), 4.53 (dt, J 5.2, 1.5 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.9, 153.9, 133.5, 130.1, 129.4, 129.0, 127.7, 125.3, 123.8, 117.3, 112.5, 69.4, 66.3, 20.5; FTIR (film) ν: 3428, 3334, 3269, 3213, 3082, 3023, 2984, 2864, 2735, 1687, 1613, 1496, 1420, 1345, 1245, 1053, 971, 806, 585 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_3Na$ [M + Na^+] 270.1106; Found 270.1103.

(*E*)-3-(2-(Allyloxy)-4-methylphenyl)allyl Carbamate (21c). Yield 6.72 g (96%) starting from 5.79 g of allyl alcohol **20c**; white solid, mp 108−109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J 7.8 Hz, 1H), 6.97 (d, J 16.0 Hz, 1H), 6.74 (d, J 7.8 Hz, 1H), 6.67 (s, 1H), 6.28 (dt, J 16.0, 6.5 Hz, 1H), 6.07 (ddt, J 17.2, 10.4, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.28 (dq, J 10.6, 1.6 Hz, 1H), 4.84−4.66 (m, 4H), 4.55 (dt, J 5.1, 1.5 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.8, 155.8, 139.2, 133.4, 129.0, 127.0, 123.0, 122.8, 121.6, 117.3, 113.2, 69.1, 66.4, 21.6; FTIR (film) ν: 3427, 3336, 3269, 3214, 3047, 3025, 2985, 2953, 2916, 1689, 1612, 1455, 1409, 1342, 1263, 1126, 1027, 973, 802 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_3Na$ [M + Na^+] 270.1106; Found 270.1105.

(*E*)-3-(2-(Allyloxy)-3-methylphenyl)allyl Carbamate (21d). Yield 6.50 g (96%) starting from 5.56 g of allyl alcohol **20d**; white solid, mp 41−42 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.31 (dd, J 7.7, 1.2 Hz, 1H), 7.11−7.07 (m, 1H), 6.98 (t, J 7.6 Hz, 1H), 6.92 (d, J 16.1 Hz, 1H), 6.28 (dt, J 16.0, 6.3 Hz, 1H), 6.14−6.03 (m, 1H), 5.42 (dq, J 17.2, 1.6 Hz, 1H), 5.26 (dq, J 10.4, 1.3 Hz, 1H), 4.90 (s, 2H), 4.73 (dd, J 6.3, 1.4 Hz, 1H), 4.29 (dt, J 5.6, 1.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.9, 155.1, 133.8, 131.6, 130.8, 129.8, 128.7, 124.6, 124.5, 124.1, 117.4, 74.2, 65.9, 16.2; FTIR (film) ν: 3475, 3354, 3195, 319, 2945, 2925, 1714, 1599, 1462, 1403, 1336, 1194, 1107, 1051, 985, 775 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_3Na$ [M + Na^+] 270.1109; Found 270.1099.

(*E*)-3-(2-(Allyloxy)-5-chlorophenyl)allyl Carbamate (21e). Yield 6.53 g (95%) starting from 5.77 g of allyl alcohol **20e**; white solid; mp 66−67 °C; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, J 2.6 Hz, 1H), 7.14 (dd, J 8.8, 2.6 Hz, 1H), 6.92 (d, J 16.1 Hz, 1H), 6.77 (d, J 8.8 Hz, 1H), 6.30 (dt, J 16.0, 6.3 Hz, 1H), 6.04 (ddt, J 17.1, 10.4, 5.2 Hz, 1H), 5.40 (dd, J 17.3, 1.5 Hz, 1H), 5.32−5.26 (m, 1H), 4.82 (s, 2H), 4.75−4.70 (m, 2H), 4.57−4.50 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.6, 154.3, 132.8, 128.4, 127.4, 127.2, 126.7, 125.9, 125.4, 117.7, 113.6, 69.5, 65.8; FTIR (film) ν: 3425, 3334, 3268, 3211, 1687, 1613, 1485, 1414, 1344, 1245 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{14}NO_3ClNa$ [M + Na^+] 290.0560; Found 290.0547.

(*E*)-3-(2-(Allyloxy)-4-chlorophenyl)allyl Carbamate (21f). Yield 1.63 g (83%) starting from 1.65 g of allyl alcohol **20f**; white solid, mp 89−90 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J 8.3 Hz, 1H), 6.93−6.82 (m, 3H), 6.29 (dt, J 16.0, 6.4 Hz, 1H), 6.05 (ddt, J 17.3, 10.6, 5.2 Hz, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.31 (dt, J 10.6, 1.4 Hz, 1H), 4.80 (s, 2H), 4.71 (dd, J 6.4, 1.3 Hz, 2H), 4.54 (dt, J 5.2, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 156.3, 134.2, 132.6, 127.9, 127.8, 124.6, 124.2, 121.0, 117.9, 112.9, 69.4, 66.0; FTIR (film) ν: 3433, 3339, 3276, 3217, 3087, 3025, 2937, 2882, 1688, 1615, 1423, 1408, 1350, 1247 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{14}ClNO_3Na$ [M + Na^+] 290.0560; Found 290.0556.

(*E*)-3-(2-(Allyloxy)-4-fluorophenyl)allyl Carbamate (21g). Yield 1.29 g (82%) starting from 1.31 g of allyl alcohol **20g**; white solid, mp 79−80 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.38 (dd, J 8.5, 6.8 Hz, 1H), 6.91 (d, J 16.0 Hz, 1H), 6.62 (td, J 8.3, 2.4 Hz, 1H), 6.58 (dd, J 10.8, 2.4 Hz, 1H), 6.25 (dt, J 16.0, 6.5 Hz, 1H), 6.05 (ddt, J 17.3, 10.6, 5.2 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.31 (dq, J 10.5, 1.4 Hz, 1H), 4.77 (s, 2H), 4.71 (dd, J 6.5, 1.3 Hz, 2H), 4.54 (dt, J 5.2, 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.4 and 162.0 (d, $J_{C\text{-}F}$ 247.1 Hz), 156.9, 156.8, and 156.7 (d, $J_{C\text{-}F}$ 9.8 Hz), 132.6, 128.13 and 128.1, (d, $J_{C\text{-}F}$ 10.1 Hz), 128.0, 123.64, and 123.61 (d, $J_{C\text{-}F}$ 2.1 Hz), 121.7, 117.9, 107.5, and 107.3 (d, $J_{C\text{-}F}$ 21.6 Hz), 100.5 and 100.2 (d, $J_{C\text{-}F}$ 25.7 Hz), 69.3, 66.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −111.1; FTIR (film) ν: 3428, 3330, 3265, 3209, 1686, 1607, 1499, 1414, 1345, 1282, 1169, 1038, 969, 928, 832, 616 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{14}NO_3FNa$ [M + Na^+] 274.0855; Found 274.0855.

(*E*)-3-(2-(Allyloxy)-5-methoxyphenyl)allyl Carbamate (21h). Yield 3.78 g (63%) starting from 5.01 g of allyl alcohol **20h**; white solid, mp 72−73 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.01−6.95 (m, 2H), 6.80 (d, J 8.9 Hz, 1H), 6.75 (dd, J 8.9, 2.9 Hz, 1H), 6.30 (dt, J 16.0, 6.4 Hz, 1H), 6.05 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.39 (dq, J 17.3, 1.6 Hz, 1H), 5.26 (dq, J 10.5, 1.4 Hz, 1H), 4.76 (s, 2H), 4.73 (dd, J 6.4, 1.4 Hz, 2H), 4.50 (dt, J 5.2, 1.5 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 153.9, 150.3, 133.6, 128.7, 126.6, 124.4, 117.3, 114.3, 114.2, 112.1, 70.2, 66.1, 55.7; FTIR (film) ν: 3476, 3357, 3208, 2942, 2835, 1713, 1496, 1337, 1215, 1042 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_4Na$ [M + Na^+] 286.1055; Found 286.1053.

(*E*)-3-(2-(Allyloxy)-3-methoxyphenyl)allyl Carbamate (21j). Yield 0.85 g (71%) starting from 1.0 g of allyl alcohol **20j**; white solid; mp 39−40 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.08 (dd, J 7.8, 1.3 Hz, 1H), 7.02−6.95 (m, 2H), 6.82 (dd, J 8.0, 1.4 Hz, 1H), 6.29 (dt, J 16.1, 6.3 Hz, 1H), 6.09 (ddt, J 17.1, 10.4, 5.9 Hz, 1H), 5.36 (dq, J 17.2, 1.6 Hz, 1H), 5.26−5.17 (m, 1H), 4.73 (dd, J 6.3, 1.4 Hz, 2H), 4.47 (dt, J 5.9, 1.3 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 153.0, 145.6, 134.2, 130.7, 128.3, 124.9, 124.8, 124.0, 118.2, 117.6, 111.8, 74.2, 65.9, 55.8; FTIR (film) ν: 3476, 3659, 3199, 2940, 2838, 1719, 1598, 1578, 1476, 1462, 1441, 1400, 1335, 1270, 1207, 1109, 1090, 1051, 984, 779, 748 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_4Na$ [M + Na^+] 286.1055; Found 286.1056.

(*E*)-3-(2-(Allyloxy)-6-methoxyphenyl)allyl Carbamate (21k). Yield 0.97 g (81%) starting from 1.0 g of allyl alcohol **20k**; white solid, mp 108−109 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.13 (t, J 8.4 Hz, 1H), 6.98 (d, J 16.2 Hz, 1H), 6.74 (dt, J 16.2, 6.5 Hz, 1H), 6.55 (d, J 8.3 Hz, 1H), 6.54 (d, J 8.4 Hz, 1H), 6.07 (ddt, J 17.2, 10.4, 5.1 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.28 (dq, J 10.6, 1.4 Hz, 1H), 4.74 (dd, J 6.5, 1.2 Hz, 2H), 4.62 (s, 2H), 4.57 (dt, J 5.1, 1.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.8, 157.6, 156.8, 133.3, 128.5, 127.3, 124.7, 117.3, 114.0, 105.3, 104.0, 69.5, 67.6, 55.7; FTIR (film) ν: 3424, 3332, 3213, 2999, 2960, 2937, 2886, 1685, 1613, 1591, 1463, 1421, 1525, 1089, 978, 770 cm^{-1}; HRMS (EI) m/z calcd for $C_{14}H_{17}NO_4$ [M] 263.1158; Found 263.1154.

(*E*)-3-(2-(Allyloxy)-5-nitrophenyl)allyl Carbamate (21l). Yield 2.86 g (85%) starting from 2.86 g of allyl alcohol **20l**; yellowish solid, mp 118−119 °C; ^1H NMR (400 MHz, DMSO-d_6) δ: 8.25 (d, J 2.8 Hz, 1H), 8.11 (dd, J 9.2, 2.8 Hz, 1H), 7.20 (d, J 9.2 Hz, 1H), 6.84 (d, J 16.2 Hz, 1H), 6.62 (s, 2H), 6.52 (dt, J 16.2, 5.7 Hz, 1H), 6.06 (ddt, J 17.3, 10.5, 5.1 Hz, 1H), 5.42 (dq, J 17.3, 1.6 Hz, 1H), 5.30 (dq, J 10.5, 1.4 Hz, 1H), 4.76 (dt, J 5.1, 1.4 Hz, 3H), 4.61 (dd, J 5.7, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 160.5, 156.9, 141.4, 133.0, 129.6, 126.3, 125.0, 124.8, 122.6, 118.6, 113.3, 69.8, 64.1; FTIR (film) v: 3347, 3202, 3087, 2935, 1712, 1512, 1341, 1260, 992 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{14}N_2O_5Na$ [M + Na^+] 301.0800; Found 301.0802.

(*E*)-3-(2-(Allyloxy)-6-methoxy-4-nitrophenyl)allyl Carbamate (21m). Yield 2.28 g (83%) starting from 2.36 g of allyl alcohol **20m**; yellow solid, mp 96−97 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, J 3.1 Hz, 1H), 7.19 (d, J 3.1 Hz, 1H), 6.86 (dt, J 16.1, 1.5 Hz, 1H), 6.34 (dt, J 16.1, 5.8 Hz, 1H), 6.04 (ddt, J 17.2, 10.4, 5.9 Hz, 1H), 5.37 (dq, J 17.2, 1.5 Hz, 1H), 5.27 (dq, J 10.4, 1.1 Hz, 1H), 4.83 (s, 2H), 4.75 (dd, J 5.8, 1.6 Hz, 2H), 4.42 (dt, J 5.9, 1.3 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 155.3, 145.1, 143.4, 134.1, 132.8, 128.1, 126.1, 119.1, 117.2, 109.0, 76.7, 65.2, 56.1; FTIR (film) ν: 3425, 3332, 3265, 3203, 3084, 2962, 2930, 2839, 1696, 1530, 1351, 1105, 1055, 975 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{16}N_2O_6Na$ [M + Na^+] 331.0906; Found 331.0897.

(*E*)-3-(2-(Allyloxy)naphthalen-1-yl)allyl Carbamate (21n). Yield 2.68 g (77%) starting from 2.96 g of allyl alcohol **20n**; white solid; mp 115−116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, J 8.5 Hz, 1H), 7.77 (d, J 8.2 Hz, 1H), 7.74 (d, J 9.0 Hz, 1H), 7.47 (ddd, J 8.4, 6.8, 1.3 Hz, 1H), 7.35 (ddd, J 7.9, 6.8, 1.0 Hz, 1H), 7.24 (d, J 9.0

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Hz, 1H), 7.09 (d, *J* 16.2 Hz, 1H), 6.38 (dt, *J* 16.2, 6.3 Hz, 1H), 6.09 (ddt, *J* 17.2, 10.3, 5.0 Hz, 1H), 5.45 (dq, *J* 17.2, 1.6 Hz, 1H), 5.29 (dq, *J* 10.6, 1.4 Hz, 1H), 4.87 (dd, *J* 6.3, 1.4 Hz, 2H), 4.83 (s, 2H), 4.68 (dt, *J* 5.0, 1.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.8, 153.6, 133.5, 132.5, 130.0, 129.3, 129.0, 128.3, 126.8, 126.6, 124.1, 123.7, 120.1, 117.3, 114.9, 70.2, 66.5; FTIR (film) *v*: 3426, 3334, 3270, 3312, 3069, 2934, 1693, 1331, 1261, 1244, 1055, 965, 805, 745 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{17}NO_3Na$ [M + Na$^+$] 306.1106; Found 306.1107.

(*E*)-3-(2-(Allyloxy)-4-methoxyphenyl)allyl Carbamate (21i). Prepared by Ichikawa's protocol.[48] A solution of allyl alcohol **20i** (220 mg, 1 mmol), phenyl carbamate (205 mg, 1.5 mmol), and dibutyltin maleate (10 mg, 0.03 mmol) in dry toluene (18 mL) was heated at 90 °C for 4.5 h. Then, the solution was diluted with 2 M NaOH and stirred for 5 min, and PhMe and water were added. The aqueous layer was additionally washed with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on Florisil to afford 135 mg (50%) of carbamate **21i** as a white solid. mp 85−86 °C; ^{1}H NMR (400 MHz, C_6D_6) δ: 7.28 (d, *J* 8.5 Hz, 1H), 7.13 (d, *J* 16.0 Hz, 1H), 6.40−6.26 (m, 3H), 5.74 (ddt, *J* 17.2, 10.4, 5.1 Hz, 1H), 5.17 (dq, *J* 17.3, 1.6 Hz, 1H), 5.00 (dq, *J* 10.6, 1.5 Hz, 1H), 4.71 (dd, *J* 6.5, 1.2 Hz, 2H), 4.18 (s, 2H), 4.08 (dt, *J* 5.0, 1.5 Hz, 2H), 3.33 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ: 160.8, 157.1, 156.5, 133.2, 128.7, 128.0, 122.5, 119.0, 116.7, 105.2, 99.9, 68.7, 66.0, 54.5; FTIR (film) *v*: 3416, 3332, 3267, 3213, 2955, 2917, 2837, 1687, 1610, 1503, 1416, 1344, 1200, 1168, 972, 834 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_4Na$ [M + Na$^+$] 286.1055; Found 286.1047.

Rearrangement of Carbamates 21 to Carbamates 24. General Procedure. To a solution of allyl carbamate **21** (0.64 mmol) and Et_3N (327 mg, 450 μL, 3.22 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (273 mg, 181 μL, 1.29 mmol), and the resulting mixture was warmed to room temperature slowly. After 1 h, dry MeOH (5 mL) and Bu_3SnOMe (0.1 mmol, 32 mg, 30 μL) were added and the reaction mixture was stirred overnight. After the removal of the solvents, the crude product was supported on silica gel and chromatographed on silica gel to afford the methyl carbamate **24**.

Methyl (1-(2-(Allyloxy)phenyl)allyl)carbamate (24a). Yield 143 mg (90%) starting from 150 mg of carbamate **21a**; white solid, mp 38−39 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26−7.19 (m, 2H), 6.93 (td, *J* 7.5, 1.1 Hz, 1H), 6.87 (d, *J* 8.2 Hz, 1H), 6.10−5.99 (m, 2H), 5.66 (s, 1H), 5.53−5.45 (m, 1H), 5.41 (dq, *J* 17.3, 1.7 Hz, 1H), 5.29 (dq, *J* 10.6, 1.4 Hz, 1H), 5.15 (dt, *J* 17.3, 1.4 Hz, 1H), 5.11 (dt, *J* 10.3, 1.4 Hz, 1H), 4.57 (dt, *J* 5.1, 1.5 Hz, 2H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 156.0, 137.9, 132.9, 128.9, 128.8(×2), 121.1, 117.6, 114.6, 112.4, 68.9, 55.1, 52.0; FTIR (film) *v*: 3440, 3331, 3061, 3015, 2986, 2952, 2922, 2867, 1722, 1495, 1241, 995, 925, 754 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_3Na$ [M + Na$^+$] 270.1106; Found 270.1096.

Methyl (1-(2-(Allyloxy)-5-methylphenyl)allyl)carbamate (24b). Yield 130 mg (82%) starting from 150 mg of carbamate **21b**; white solid, mp 56−57 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.04−7.02 (m, 2H), 6.77 (d, *J* 8.4 Hz, 1H), 6.10−5.98 (m, 2H), 5.68 (br s, 1H), 5.46−5.37 (m, 2H), 5.30−5.26 (m, 1H), 5.16 (d, *J* 17.2 Hz, 1H), 5.10 (d, *J* 10.3 Hz, 1H), 4.54 (d, *J* 5.0 Hz, 2H), 3.66 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.3, 153.9, 138.0, 133.1, 130.4, 129.6, 129.0, 128.7, 117.5, 114.5, 112.5, 69.1, 55.3, 52.0, 20.4; FTIR (film) *v*: 3440, 3334, 3084, 3015, 2985, 2954, 2922, 2864, 1723, 1501, 1244, 1032, 995, 923, 808 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_3Na$ [M + Na$^+$] 284.1263; Found 284.1263.

Methyl (1-(2-(Allyloxy)-4-methylphenyl)allyl)carbamate (24c). Yield 156 mg (98%) starting from 150 mg of carbamate **21c**; white solid, mp 44−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08 (d, *J* 7.6 Hz, 1H), 6.76−6.72 (m, 1H), 6.70 (s, 1H), 6.10−5.98 (m, 2H), 5.49−5.37 (m, 2H), 5.29 (dq, *J* 10.6, 1.4 Hz, 1H), 5.15 (dt, *J* 17.2, 1.4 Hz, 1H), 5.09 (dt, *J* 10.3, 1.4 Hz, 1H), 4.55 (dt, *J* 5.1, 1.5 Hz, 2H), 3.66 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 155.9, 138.9, 138.1, 133.0, 128.7, 126.0, 121.6, 117.5, 114.4, 113.3, 68.9, 54.9, 52.0, 21.5; FTIR (film) v: 3442, 3334, 3084, 3015, 2984, 2952, 2922, 2861, 1725, 1505, 1261, 1031, 924 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_3Na$ [M + Na$^+$] 284.1263; Found 284.1263.

Methyl (1-(2-(Allyloxy)-3-methylphenyl)allyl)carbamate (24d). Yield 157 mg (97%) starting from 150 mg of carbamate **21d**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14−6.98 (m, 3H), 6.12 (ddt, *J* 16.0, 10.7, 5.5 Hz, 1H), 5.99 (ddd, *J* 17.2, 10.5, 4.6 Hz, 1H), 5.63−5.58 (m, 1H), 5.45 (dq, *J* 17.2, 1.6 Hz, 1H), 5.28 (dq, *J* 10.5, 1.3 Hz, 1H), 5.18−5.10 (m, 2H), 4.50−4.41 (m, 1H), 4.34 (ddt, *J* 12.4, 5.5, 1.4 Hz, 2H), 3.66 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 155.1, 138.5, 133.9, 133.7, 131.7, 130.9, 125.8, 124.3, 117.4, 114.7, 73.9, 52.9, 52.1, 16.5; FTIR (film) *v*: 3422, 3332, 3015, 2952, 1710, 1511, 1466, 1248, 1193, 989, 924 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_3Na$ [M + Na$^+$] 284.1263; Found 284.1258.

Methyl (1-(2-(Allyloxy)-5-chlorophenyl)allyl)carbamate (24e). Yield 123 mg (78%) starting from 150 mg of carbamate **21e**; white solid, mp 65−66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.21−7.14 (m, 2H), 6.80 (d, *J* 9.0 Hz, 1H), 6.10−5.89 (m, 2H), 5.56−5.44 (m, 2H), 5.40 (dq, *J* 17.4, 1.2 Hz, 1H), 5.29 (dq, *J* 10.7, 1.1 Hz, 1H), 5.18−5.11 (m, 2H), 4.55 (d, *J* 5.1 Hz, 2H), 3.67 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.1, 154.5, 137.1, 132.5, 130.8, 128.5, 128.4, 125.9, 117.9, 115.3, 113.6, 69.3, 54.2; FTIR (film) *v*: 3438, 3328, 3085, 3015, 2986, 2952, 1708, 1508, 1488, 1283, 1246, 1192, 1086, 995, 926, 808 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{16}NO_3ClNa$ [M + Na$^+$] 304.0716; Found 304.0717.

Methyl (1-(2-(Allyloxy)-4-chlorophenyl)allyl)carbamate (24f). Yield 133 mg (84%) starting from 150 mg of carbamate **21f**; white solid, mp 68−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.12 (d, *J* 8.1 Hz, 1H), 6.90 (dd, *J* 8.1, 1.9 Hz, 1H), 6.85 (d, *J* 1.9 Hz, 1H), 6.06−5.94 (m, 2H), 5.55 (s, 1H), 5.49−5.44 (m, 1H), 5.40 (dq, *J* 17.3, 1.3 Hz, 1H), 5.30 (dq, *J* 10.6, 1.1 Hz, 1H), 5.15−5.09 (m, 2H), 4.54 (dt, *J* 5.1, 1.5 Hz, 2H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.5, 156.2, 137.3, 134.1, 132.3, 129.4, 127.7, 121.0, 118.0, 115.0, 113.0, 69.2, 54.1, 52.1; FTIR (film) *v*: 3441, 3331, 3085, 2986, 2953, 1722, 1714, 1596, 1489, 1408, 1245, 1091, 998, 926, 897 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd form $C_{14}H_{16}NO_3ClNa$ [M + Na$^+$] 304.0716; Found 304.0713.

Methyl (1-(2-(Allyloxy)-4-fluorophenyl)allyl)carbamate (24g). Yield 142 mg (90%) starting from 150 mg of carbamate **21g**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16−7.11 (m, 1H), 6.62−6.56 (m, 2H), 5.99 (ddt, *J* 17.2, 10.4, 5.1 Hz, 2H), 5.57 (s, 1H), 5.50−5.44 (m, 1H), 5.39 (dq, *J* 17.3, 1.5 Hz, 1H), 5.28 (dq, *J* 10.6, 1.3 Hz, 1H), 5.15−5.07 (m, 2H), 4.51 (dt, *J* 5.1, 1.5 Hz, 2H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.2 and 161.7 (d, $J_{C\text{-}F}$ 245.7 Hz), 157.0 and 156.9 (d, $J_{C\text{-}F}$ Hz), 156.2, 137.6, 132.3, 129.5, and 129.4 (d, $J_{C\text{-}F}$ 9.8 Hz), 124.91 and 124.87 (d, $J_{C\text{-}F}$ 3.2 Hz), 117.9, 114.8, 107.2, and 107.0 (d, $J_{C\text{-}F}$ 21.2 Hz), 100.8 and 100.5 (d, $J_{C\text{-}F}$ 25.8 Hz), 69.1, 54.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.0; FTIR (film) *v*: 3445, 3330, 3085, 2987, 2953, 1712, 1609, 1501, 1281, 1249, 1025, 926, 835 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{16}NO_3FNa$ [M + Na$^+$] 288.1012; Found 288.1014.

Methyl (1-(2-(Allyloxy)-5-methoxyphenyl)allyl)carbamate (24h). Yield 139 mg (88%) starting from 150 mg of carbamate **21h**; waxy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.82−6.70 (m, 3H), 6.08−5.95 (m, 2H), 5.70 (s, 1H), 5.47−5.41 (m, 1H), 5.38 (dq, *J* 17.3, 1.4 Hz, 1H), 5.25 (dq, *J* 10.6, 1.2 Hz, 1H), 5.14 (d, *J* 17.2 Hz, 1H), 5.10 (d, *J* 10.3 Hz, 1H), 4.52−4.47 (m, 2H), 3.73 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 153.9, 150.1, 137.8, 133.2, 130.2, 117.4, 114.9, 114.7, 113.7, 113.0, 69.7, 55.6, 55.0, 52.0; FTIR (film) *v*: 3437, 3335, 3083, 2990, 2952, 2911, 2836, 1727, 1500, 1240, 1216, 1042 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_4Na$ [M + Na$^+$] 300.1212; Found 300.1210.

Methyl (1-(2-(Allyloxy)-4-methoxyphenyl)allyl)carbamate (24i). Yield 138 mg (87%) starting from 150 mg of carbamate **21i**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (d, *J* 8.4 Hz, 1H), 6.46−6.42 (m, 2H), 6.08−5.97 (m, 2H), 5.60−5.52 (m, 1H), 5.41 (s, 1H), 5.41 (dq, *J* 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* 10.6, 1.4 Hz, 1H), 5.17−5.07 (m, 2H), 4.53 (dt, *J* 5.1, 1.5 Hz, 2H), 3.77 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.4, 157.0, 156.3, 138.2, 132.8, 129.4, 121.5, 117.7, 114.3, 104.5, 100.4, 68.9, 55.4, 54.6, 52.0; FTIR

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(film) ν: 3440, 3339, 3083, 2952, 1723, 1504, 1258, 1200, 1166 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}NO_4Na$ [M + Na^+] 300.1212; Found 300.1210.

Methyl (1-(2-(Allyloxy)-3-methoxyphenyl)allyl)carbamate (24j). Yield 132 mg (84%) starting from 150 mg of carbamate **21j**; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 6.99 (t, J 7.9 Hz, 1H), 6.83 (dd, J 8.2, 1.4 Hz, 1H), 6.79 (d, J 7.7 Hz, 1H), 6.09 (ddt, J 16.3, 10.9, 5.7 Hz, 1H), 5.97 (ddd, J 16.9, 10.4, 4.6 Hz, 1H), 5.65 (s, 1H), 5.52 (ddt, J 8.7, 4.3, 1.8 Hz, 1H), 5.36 (dq, J 17.2, 1.5 Hz, 1H), 5.22 (dq, J 10.4, 1.3 Hz, 1H), 5.14−5.08 (m, 2H), 4.63−4.57 (m, 1H), 4.51−4.45 (m, 1H), 3.81 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 152.9, 145.5, 138.3, 134.5, 134.2, 124.2, 120.2, 117.5, 114.6, 112.0, 73.7, 55.7, 53.8, 52.0; FTIR (film) ν: 3427, 3334, 3083, 3007, 2953, 2840, 1709, 1508, 1477, 1269, 1239, 1086, 989, 926 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}NO_4Na$ [M + Na^+] 300.1212; Found 300.1211.

Methyl (1-(2-(Allyloxy)-6-methoxyphenyl)allyl)carbamate (24k). Yield 143 mg (90%) starting from 150 mg of carbamate **21k**; colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.15 (t, J 8.4 Hz, 1H), 6.54 (d, J 8.3 Hz, 1H), 6.53 (d, J 8.3 Hz, 1H), 6.19 (d, J 9.8 Hz, 1H), 6.12−5.96 (m, 3H), 5.41 (dq, J 17.3, 1.5 Hz, 1H), 5.27 (dq, J 10.6, 1.3 Hz, 1H), 5.12 (d, J 17.0 Hz, 1H), 5.01 (d, J 10.1 Hz, 1H), 4.54 (d, J 5.1 Hz, 2H), 3.81 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.8, 156.7, 156.4, 138.0, 133.0, 128.7, 117.5, 117.2, 113.7, 105.8, 104.6, 69.4, 55.9, 51.9, 48.6; FTIR (film) ν: 3445, 3083, 3007, 2981, 2840, 1726, 1595, 1502, 1471, 1250, 1100, 781 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{19}NO_4Na$ [M + Na^+] 300.1212; Found 300.1212.

Methyl (1-(2-(Allyloxy)-5-nitrophenyl)allyl)carbamate (24l). Yield 156 mg (97%) starting from 150 mg of carbamate **21l**; white solid; mp 118−119 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.17−8.05 (m, 3H), 6.91 (d, J 9.7 Hz, 1H), 6.05−5.92 (m, 2H), 5.66−5.53 (m, 2H), 5.40 (dq, J 17.3, 1.5 Hz, 1H), 5.31 (dq, J 10.6, 1.2 Hz, 1H), 5.19−5.09 (m, 2H), 4.66 (dt, J 5.1, 1.4 Hz, 2H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.7, 156.1, 141.4, 136.2, 131.6, 130.5, 125.0, 123.8, 118.6, 116.1, 111.8, 69.6, 53.1, 52.3; FTIR (film) ν: 3323, 3086, 2952, 1705, 1518, 1341, 1267, 1237, 1088, 994, 927, 829, 755 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{16}N_2O_5Na$ [M + Na^+] 315.0957; Found 315.0949.

Methyl (1-(2-(Allyloxy)-6-methoxy-4-nitrophenyl)allyl)-carbamate (24m). Yield 132 mg (84%) starting from 150 mg of carbamate **21m**; brown oil; ^1H NMR (400 MHz, CDCl3) δ: 7.24 (d, J 3.2 Hz, 1H), 7.04 (d, J 3.2 Hz, 1H), 6.05 (ddt, J 16.3, 10.5, 5.8 Hz, 1H), 5.92 (ddd, J 17.1, 10.4, 5.0 Hz, 1H), 5.63−5.58 (m, 1H), 5.45 (d, J 6.6 Hz, 1H), 5.38 (dq, J 17.2, 1.5 Hz, 1H), 5.26 (dq, J 10.4, 1.3 Hz, 1H), 5.21−5.17 (m, 1H), 5.12 (dd, J 17.2, 1.3 Hz, 1H), 4.58−4.45 (m, 2H), 3.79 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 155.3, 144.3, 143.6, 138.8, 136.7, 132.7, 119.5, 118.9, 116.4, 108.5, 76.3, 56.0, 52.4; FTIR (film) v: 3327, 3088, 3011, 2984, 2953, 2843, 1706, 1534, 1351, 1241, 1213, 1052, 981, 932, 782 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{18}N_2O_6Na$ [M + Na^+] 345.1063; Found 345.1058.

Methyl (1-(2-(Allyloxy)naphthalen-1-yl)allyl)carbamate (24n). Yield 114 mg (72%) starting from 150 mg of carbamate **21n**; white solid, mp 58−59 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.21 (d, J 8.6 Hz, 1H), 7.83−7.74 (m, 2H), 7.58−7.48 (m, 1H), 7.37 (t, J 7.5 Hz, 1H), 7.25 (d, J 9.0 Hz, 1H), 6.37 (d, J 16.5 Hz, 2H), 6.24−6.03 (m, 2H), 5.52−5.43 (m, 1H), 5.36−5.32 (m, 1H), 5.20 (d, J 17.1 Hz, 1H), 5.11 (d, J 10.2 Hz, 1H), 4.69 (q, J 7.7, 6.6 Hz, 2H), 3.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 154.1, 138.1, 133.0, 131.8, 129.6, 129.5, 128.6, 127.2, 123.9, 122.7, 122.0, 118.2, 114.7, 114.3, 70.1, 52.1, 50.6; FTIR (film) ν: 3444, 3354, 3079, 3013, 2983, 2952, 1724, 1504, 1322, 1254, 1239, 1084, 992, 857, 745 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}NO_3Na$ [M + Na^+] 320.1263; Found 320.1253.

***t*-Butyl (1-(2-(Allyloxy)phenyl)allyl)carbamate (24o).** To a solution of allyl carbamate **21a** (150 mg, 0.64 mmol) and Et_3N (327 mg, 450 μL, 3.22 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (273 mg, 181 μL, 1.29 mmol), and the resulting mixture was warmed to room temperature slowly. In a separate flask, a 1 M soln. of LiHMDS in THF (3.2 mL, 3.22 mmol) was added to a solution of *t*-BuOH (0.62 mL) in dry THF (10 mL). After 1 h, the solution of *t*-BuOLi was added to the generated allyl isocyanate, and the reaction mixture was stirred for 2 h. Then, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (20% AcOEt in hexanes) to afford 141 mg of compound **24o** (76%) as a waxy solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.27−7.19 (m, 2H), 6.93 (t, J 7.3 Hz, 1H), 6.87 (d, J 8.1 Hz, 1H), 6.10−6.00 (m, 2H), 5.48 (s, 1H), 5.42 (dd, J 17.2, 1.3 Hz, 1H), 5.28 (dd, J 10.5, 1.3 Hz, 1H), 5.15 (br d, J 17.2 Hz, 1H), 5.10 (d, J 10.3 Hz, 1H), 4.60−4.55 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.9, 155.1, 138.2, 133.0, 130.0, 129.3, 128.6, 120.9, 117.4, 114.3, 112.3, 79.2, 68.8, 54.1, 28.4; FTIR (film) ν: 3450, 3350, 3082, 2978, 2930, 2871, 1712, 1491, 1366, 1244, 1170, 753 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{23}NO_3Na$ [M + Na^+] 312.1576; Found 312.1574.

Benzyl (1-(2-(Allyloxy)phenyl)allyl)carbamate (24p). To a solution of allyl carbamate **21a** (0.64 mmol) and Et_3N (327 mg, 450 μL, 3.22 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (273 mg, 181 μL, 1.29 mmol), and the resulting mixture was warmed to room temperature slowly. In a separate flask, a 1 M soln. of LiHMDS in THF (3.2 mL, 3.22 mmol) was added to a solution of BnOH (400 μL, 3.22 mmol) in dry THF (10 mL). After 1 h, the solution of BnOLi was added to the generated allyl isocyanate, and the reaction mixture was stirred overnight. Then, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (AcOEt/hexanes 1:8) to afford 176 mg of **24p** (85%) as a yellowish oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.28−7.23 (m, 3H), 7.21−7.09 (m, 4H), 6.83 (td, J 7.5, 0.9 Hz, 1H), 6.78 (d, J 8.1 Hz, 1H), 6.02−5.92 (m, 2H), 5.60 (d, J 8.9 Hz, 1H), 5.54−5.48 (m, 1H), 5.33 (dq, J 17.3, 1.5 Hz, 1H), 5.20 (dq, J 10.6, 1.3 Hz, 1H), 5.02−4.91 (m, 2H), 4.58 (s, 2H), 4.49−4.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.0, 155.7, 137.9, 136.7, 133.0, 128.9, 128.6, 128.5, 128.3, 128.1, 128.0, 121.1, 117.6, 114.7, 112.5, 68.9, 66.7, 55.0; FTIR (film) ν: 3461, 3347, 2976, 1631, 1511, 1491, 1267, 1237, 1225, 1195, 966, 754 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{21}NO_3Na$ [M + Na^+] 346.1419; Found 346.1422.

***N*-(1-(2-(Allyloxy)phenyl)allyl)acetamide (24q).** To a solution of allyl carbamate **21a** (150 mg, 0.64 mmol) and Et_3N (327 mg, 450 μL, 3.22 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (273 mg, 181 μL, 1.29 mmol), and the resulting mixture was warmed to room temperature slowly. After 1 h, the reaction mixture was cooled to −10 °C and a 3 M soln. of MeMgBr in Et_2O (1.3 mL, 3.86 mmol) was added dropwise. After stirring at −10 °C for 30 min, the reaction mixture was warmed to room temperature and stirred at that temperature for an additional 2 h. Next, the reaction mixture was poured onto sat. aq. NH_4Cl and extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was chromatographed on silica gel (50% AcOEt in hexanes) to afford 135 mg of **24q** (91%) as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.16 (m, 2H), 6.94−6.86 (m, 2H), 6.73 (s, 1H), 6.10−5.96 (m, 2H), 5.79−5.73 (m, 1H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.29 (dq, J 10.6, 1.4 Hz, 1H), 5.14−5.05 (m, 2H), 4.57 (dt, J 5.1, 1.5 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.6, 156.1, 137.4, 132.9, 129.5, 128.9, 128.4, 121.3, 117.7, 114.8, 112.4, 68.9, 53.7, 23.2; FTIR (film) v: 3433, 3286, 3082, 1654, 1492, 1209, 1144, 755 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{17}NO_2Na$ [M + Na^+] 254.1157; Found 254.1154.

***N*-(1-(2-(Allyloxy)phenyl)allyl)benzamide (24r).** Prepared in the same manner as compound **24q**; yield 145 mg (77%) starting from 150 mg of carbamate **21a**; yellowish solid, mp 90−91 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.81−7.77 (m, 2H), 7.50−7.37 (m, 4H), 7.31 (dd, J 7.5, 1.6 Hz, 1H), 7.29−7.24 (m, 1H), 6.96 (td, J 7.5, 1.0 Hz, 1H), 6.92 (d, J 8.2 Hz, 1H), 6.21−6.04 (m, 1H), 6.00−5.92 (m, 1H), 5.47 (dq, J 17.3, 1.5 Hz, 1H), 5.33 (dq, J 10.5, 1.3 Hz, 1H), 5.20 (dt, J 17.1, 1.4 Hz, 1H), 5.15 (dt, J 10.2, 1.4 Hz, 1H), 4.66−4.52 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 156.2, 137.7, 134.7, 132.9, 131.3, 129.6, 129.0, 128.5(×2), 127.0, 121.4, 118.1, 114.9, 112.4, 69.0, 54.3; FTIR (film) ν: 3439, 3321, 3063, 1640, 1525, 1488, 1243, 995, 924, 754, 694 cm^{-1}; HRMS (ESI-TOF) m/z $C_{19}H_{19}NO_2Na$ [M + Na^+] 316.1313; Found 316.1310.

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1-(1-(2-(Allyloxy)phenyl)allyl)-3-benzylurea (24s). To a solution of allyl carbamate **21a** (150 mg, 0.64 mmol) and Et_3N (327 mg, 450 μL, 3.22 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (273 mg, 181 μL, 1.29 mmol), and the resulting mixture was warmed to room temperature slowly. After stirring for 1.5 h, $BnNH_2$ (413 mg, 420 μL, 3.86 mmol) was added, and the reaction mixture was stirred overnight. Then, the reaction mixture was diluted with AcOEt (50 mL) and washed with 1 M HCl (10 mL), water (15 mL), and brine (15 mL). After drying over anhydrous Na_2SO_4, the solvents were removed and the residue was purified by flash chromatography on silica gel (20% to 50% AcOEt in hexanes) to afford 142 mg of **24s** (68%) as a white solid; mp 96−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28−7.15 (m, 7H), 6.89 (t, *J* 7.1 Hz, 1H), 6.82 (d, *J* 8.3 Hz, 1H), 6.03−5.90 (m, 2H), 5.78−5.70 (m, 1H), 5.68−5.61 (m, 1H), 5.47−5.39 (m, 1H), 5.39−5.31 (m, 2H), 5.24−5.19 (m, 2H), 5.12 (d, *J* 17.2 Hz, 1H), 5.06 (d, *J* 10.3 Hz, 1H), 4.52−4.42 (m, 2H), 4.30−4.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.8, 155.7, 139.4, 138.5, 133.1, 129.8, 128.5, 128.4, 128.4, 127.3, 127.0, 121.1, 117.4, 114.4, 112.3, 68.9, 52.7, 44.3; FTIR (film) *v*: 3338, 3083, 3029, 2921, 2868, 1630, 1563, 1491, 1239, 752 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{22}N_2O_2Na$ [M + Na$^+$] 345.1579; Found 345.1577.

***N*-(1-(2-(Allyloxy)phenyl)allyl)morpholine-4-carboxamide (24t).** Prepared in the same manner as compound **24s**; yield 172 mg (89%) starting from carbamate **21a**; white solid, mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (t, *J* 7.6 Hz, 2H), 6.91 (t, *J* 7.4 Hz, 1H), 6.86 (d, *J* 8.0 Hz, 1H), 6.12−5.97 (m, 2H), 5.83 (d, *J* 8.6 Hz, 1H), 5.66−5.56 (m, 1H), 5.46−5.36 (m, 1H), 5.31−5.23 (m, 1H), 5.11−5.01 (m, 2H), 4.59−4.49 (m, 2H), 3.68−3.57 (m, 4H), 3.35−3.26 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.9, 156.1, 138.7, 133.0, 129.5, 129.3, 128.7, 121.3, 117.8, 114.3, 112.3, 68.8, 66.5, 55.5, 43.9; FTIR (film) *v*: 3453, 3345, 3079, 2962, 2918, 2695, 2855, 1630, 1524, 1491, 1246, 1118, 997, 754 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{22}N_2O_3Na$ [M + Na$^+$] 325.1528; Found 325.1530.

Ring-Closing Metathesis of Dienes 24. General Procedure. A solution of diene (0.19 mmol) and Grubbs 2nd gen. catalyst (8.5 mg, 10 μmol, 5 mol %) in degassed dichloroethane (5 mL) was kept at 50 °C for 2−4 h. Next, the solvent was removed and the product was isolated by flash column chromatography.

Methyl (2,5-Dihydrobenzo[*b*]oxepin-5-yl)carbamate (25a). Yield 37 mg (84%) starting from 50 mg of carbamate **24a**; white solid; mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28−7.21 (m, 2H), 7.12−7.04 (m, 2H), 6.05−5.97 (m, 1H), 5.57 (d, *J* 11.5 Hz, 2H), 5.34−5.23 (m, 1H), 4.68 (br d, *J* 17.5 Hz, 1H), 4.42 (br d, *J* 17.5 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.2, 156.1, 136.7, 129.8, 129.3, 127.9, 127.7, 124.7, 121.9, 70.9, 52.1, 51.4; FTIR (film) *v*: 3326, 3028, 2950, 2844, 1719, 1515, 1492, 1268, 1226, 1069, 1042, 1025, 759 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{13}NO_3Na$ [M + Na$^+$] 242.0793; Found 242.0791.

Methyl (7-Methyl-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25b). Yield 37 mg (83%) starting from 50 mg of carbamate **24b**; white solid, mp 145−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07−7.00 (m, 2H), 6.96 (d, *J* 8.0 Hz, 1H), 6.09−5.94 (m, 1H), 5.66−5.51 (m, 2H), 5.26−5.16 (m, 1H), 4.66 (d, *J* 17.5 Hz, 1H), 4.38 (d, *J* 17.4 Hz, 1H), 3.64 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 154.9, 136.3, 134.3, 129.9, 129.6, 128.5, 127.7, 121.5, 71.0, 52.1, 51.4, 20.8; IR (film) *v*: 3329, 3026, 2950, 2925, 2843, 1721, 1496, 1268, 1228, 1040, 829 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{15}NO_3$ [M] 233.1052; Found 233.1053.

Methyl (8-Methyl-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25c). Yield 42 (94%) starting from 50 mg of carbamate **24c**; white solid, mp 111−112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.14 (d, *J* 7.7 Hz, 1H), 6.97−6.81 (m, 2H), 6.07−5.96 (m, 1H), 5.62−5.49 (m, 2H), 5.29−5.16 (m, 1H), 4.68 (br d, *J* 17.0 Hz, 1H), 4.41 (br d, *J* 17.0 Hz, 1H), 3.64 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.0, 156.1, 139.5, 133.5, 129.8, 127.8, 125.2, 122.5, 70.9, 52.1, 51.2, 21.0; FTIR (film) *v*: 3328, 3026, 2951, 2926, 2845, 1720, 1503, 1272, 1238, 1073, 1042, 778 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_3Na$ [M + Na$^+$] 256.0950; Found 256.0950.

Methyl (9-Methyl-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25d). Yield 32 mg (72%) starting from 50 mg of carbamate **24d**; white solid, mp 70−71 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.84 (d, *J* 8.8 Hz, 1H), 7.11−7.07 (m, 1H), 6.96 (t, *J* 7.5 Hz, 1H), 6.91 (d, *J* 7.5 Hz, 1H), 5.77−5.71 (m, 1H), 5.69−5.63 (m, 1H), 5.42 (dq, *J* 11.5, 2.5 Hz, 1H), 4.69 (dq, *J* 17.5, 2.9 Hz, 1H), 4.27 (dq, *J* 17.5, 2.4 Hz, 1H), 3.55 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 154.9, 136.6, 130.8, 130.7, 129.6, 127.9, 125.4, 124.4, 69.4, 52.1, 51.3, 15.4; FTIR (film) *v*: 3326, 2951, 2925, 1721, 1512, 1470, 1271, 1232, 1190 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_3Na$ [M + Na$^+$] 256.0950; Found 256.0948.

Methyl (7-Chloro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25e). Yield 36 mg (80%) starting from 50 mg of carbamate **24e**; white solid, mp 102−104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24−7.14 (m, 2H), 6.99 (d, *J* 8.4 Hz, 1H), 5.91 (d, *J* 6.9 Hz, 1H), 5.55 (d, *J* 10.6 Hz, 2H), 5.35−5.23 (m, 1H), 4.63 (br d, *J* 17.5 Hz, 1H), 4.42 (br d, *J* 17.5 Hz, 1H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.7, 156.1, 155.6, 138.4, 129.7, 129.0, 127.5, 127.3, 123.3, 71.0, 52.3, 50.8; FTIR (film) *v*: 3336, 3030, 2952, 2744, 1705, 1515, 1480, 1269, 1229, 1069, 1040, 828 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{12}NO_3ClNa$ [M + Na$^+$] 276.0403; Found 276.0399.

Methyl (8-Chloro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25f). Yield 34 mg (75%) starting from 50 mg of carbamate **24f**; white solid, mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (d, *J* 8.0 Hz, 1H), 7.09 (d, *J* 2.1 Hz, 1H), 7.06 (dd, *J* 8.0, 2.1 Hz, 1H), 6.00−5.94 (m, 1H), 5.58 (dt, *J* 11.8, 2.7 Hz, 1H), 5.53−5.49 (m, 1H), 5.26 (t, *J* 8.2 Hz, 1H), 4.67 (br d, *J* 17.5 Hz, 1H), 4.43 (br d, *J* 17.5 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.7, 156.0, 135.3, 134.0, 129.7, 128.9, 127.3, 124.8, 122.6, 71.0, 52.2, 50.9; FTIR (film) *v*: 3420, 3323, 3028, 2952, 2925, 2853, 1708, 1520, 1481, 1270, 1226, 1075 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{12}NO_3ClNa$ [M + Na$^+$] 276.0403; Found 276.0401.

Methyl (8-Fluoro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25g). Yield 36 mg (80%) starting from 50 mg of carbamate **24g**; waxy solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19−7.08 (m, 1H), 6.77−6.65 (m, 2H), 5.93−5.85 (m, 1H), 5.52−5.39 (m, 2H), 5.21−5.12 (m, 1H), 4.59 (br d, *J* 17.4 Hz, 1H), 4.34 (br d, *J* 17.4 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.1 and 161.6 (d, J_{C-F} 247.6 Hz), 158.3 and 158.2 (d, J_{C-F} 10.8 Hz), 156.2, 132.8 (d, J_{C-F} 2.6 Hz), 129.6, 129.1, and 129.0 (d, J_{C-F} 9.4 Hz), 127.7, 111.5, and 111.2 (d, J_{C-F} 21.1 Hz), 110.0 and 109.8 (d, J_{C-F} 22.7 Hz), 71.0, 52.3, 51.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −112.3; FTIR (film) *v*: 3323, 3029, 2952, 2847, 1706, 1603, 1496, 1264, 1238, 1144, 1097 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{12}NO_3FNa$ [M + Na$^+$] 260.0699; Found 260.0700.

Methyl (8-Methoxy-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25h). Yield 36 mg (80%) starting from 50 mg of carbamate **24h**; white solid, mp 97−99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* 8.1 Hz, 1H), 6.65−6.60 (m, 2H), 6.05−5.98 (m, 1H), 5.57 (d, *J* 11.3 Hz, 1H), 5.50 (d, *J* 8.6 Hz, 1H), 5.22−5.15 (m, 1H), 4.68 (br d, *J* 17.4 Hz, 1H), 4.41 (br d, *J* 17.4 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 160.5, 158.2, 156.1, 129.5, 128.9, 128.8, 127.9, 109.6, 108.0, 70.9, 55.4, 52.1, 51.1; FTIR (film) v: 3331, 3023, 3000, 2952, 2917, 2840, 1716, 1613, 1500, 1269, 1238, 1158, 1107, 1031 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_4Na$ [M + Na$^+$] 272.0899; Found 272.0900.

Methyl (7-Methoxy-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25i). Yield 35 mg (78%) starting from 50 mg of carbamate **24i**; white solid, mp 108−110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.99 (d, *J* 8.7 Hz, 1H), 6.79 (s, 1H), 6.72 (dd, *J* 8.7, 3.0 Hz, 1H), 6.04−5.96 (m, 1H), 5.61 (d, *J* 9.0 Hz, 1H), 5.54 (d, *J* 11.5 Hz, 1H), 5.29−5.17 (m, 1H), 4.63 (br d, *J* 17.4 Hz, 1H), 4.38 (br d, *J* 17.3 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 156.1, 150.7, 137.6, 130.0, 127.6, 122.4, 113.7, 113.2, 71.1, 55.6, 52.1, 51.3; FTIR (film) v: 3328, 3024, 2999, 2952, 2839, 1715, 1496, 1267, 1202, 1034 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_4Na$ [M + Na$^+$] 272.0899; Found 272.0898.

Methyl (9-Methoxy-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25j). Yield 36 mg (80%) starting from 50 mg of carbamate **24j**; white solid; mp 112−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04−7.00 (m, 1H), 6.87 (dd, *J* 8.3, 1.4 Hz, 1H), 6.84 (d, *J* 7.8 Hz, 1H), 6.03−5.96 (m, 1H), 5.63 (d, *J* 9.2 Hz, 1H), 5.55 (d, *J* 11.5 Hz,

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1H), 5.31−5.25 (m, 1H), 4.70 (d, *J* 17.5 Hz, 1H), 4.42 (d, *J* 17.5 Hz, 1H), 3.85 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 152.2, 145.3, 138.4, 129.8, 127.6, 124.9, 119.4, 112.1, 70.1, 56.0, 52.1, 51.1; FTIR (film) *v*: 3326, 3024, 3000, 2949, 2840, 1720, 1527, 1484, 1279, 1095, 1040, 739 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_4Na$ [M + Na$^+$] 272.0899; Found 272.0891.

Methyl (6-Methoxy-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25k). Yield 37 mg (82%) starting from 50 mg of carbamate **24k**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (t, *J* 8.2 Hz, 1H), 6.71−6.68 (m, 2H), 6.19−6.11 (m, 1H), 5.83−5.70 (m, 2H), 5.53 (ddd, *J* 11.4, 3.7, 1.8 Hz, 1H), 4.75 (ddd, *J* 17.5, 3.7, 2.0 Hz, 1H), 4.32 (dt, *J* 17.5, 2.3 Hz, 1H), 3.84 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.7, 156.1, 129.7, 129.2(×2), 128.0, 125.5, 114.1, 107.9, 71.1, 56.2, 52.0, 42.4; FTIR (film) *v*: 3419, 3356, 3023, 3000, 2952, 2936, 2841, 1721, 1601, 1500, 1472, 1278, 1243, 1219, 1091, 1030, 731 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_4Na$ [M + Na$^+$] 272.0899; Found 272.0908.

Methyl (7-Nitro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25l). Yield 36 mg (80%) starting from 50 mg of carbamate **24l**; white solid; mp 150−150 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.18 (d, *J* 8.6 Hz, 1H), 8.14 (dd, *J* 8.7, 2.8 Hz, 1H), 7.96 (d, *J* 2.8 Hz, 1H), 7.31 (d, *J* 8.7 Hz, 1H), 5.87−5.81 (m, 1H), 5.78−5.68 (m, 1H), 5.54 (dq, *J* 11.7, 2.8 Hz, 1H), 4.91 (dq, *J* 17.2, 3.1 Hz, 1H), 4.42 (dq, *J* 17.3, 2.6 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 162.2, 156.0, 144.4, 138.2, 129.1, 127.5, 125.0, 123.0, 122.9, 71.0, 52.4, 50.6; FTIR (film) v: 3293, 3078, 2952, 2847, 1701, 1523, 1346, 1270, 1236, 1066 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{12}N_2O_5Na$ [M + Na$^+$] 287.0644; Found 287.0634.

Methyl (6-Methoxy-8-nitro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (25m). Yield 37 mg (81%) starting from 50 mg of carbamate **24m**; white solid, mp 138−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, *J* 3.1 Hz, 1H), 7.05 (d, *J* 3.1 Hz, 1H), 5.99−5.91 (m, 1H), 5.63 (br d, *J* 11.5 Hz, 1H), 5.54 (br d, J 9.5 Hz, 1H), 5.38−5.32 (m, 1H), 4.78 (br d, *J* 17.8 Hz, 1H), 4.66 (br d, *J* 17.8 Hz, 1H), 3.81 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.0, 155.6, 144.0, 143.2, 141.2, 130.0, 126.5, 118.7, 107.8, 71.3, 56.0, 52.3, 51.0; FTIR (film) *v*: 3322, 2952, 2924, 2852, 1706, 1534, 1482, 1357, 1321, 1264, 1230, 1214, 1076, 1052, 1006, 780 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{14}N_2O_6Na$ [M + Na$^+$] 317.0750; Found 317.0741.

Methyl (1,4-Dihydronaphtho[2,1-*b*]oxepin-1-yl)carbamate (25n). Yield 39 mg (86%) starting from 50 mg of carbamate **24n**; white solid, mp 141−142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* 8.6 Hz, 1H), 7.82 (d, *J* 8.2 Hz, 1H), 7.79 (d, *J* 8.7 Hz, 1H), 7.57 (t, *J* 7.3 Hz, 1H), 7.48−7.40 (m, 1H), 7.27 (d, *J* 9.0 Hz, 1H), 6.29−6.21 (m, 2H), 6.13 (t, *J* 9.0 Hz, 1H), 5.96 (d, *J* 9.2 Hz, 1H), 5.64 (ddd, *J* 11.3, 3.6, 1.7 Hz, 1H), 4.83 (ddd, *J* 17.4, 3.6, 1.9 Hz, 1H), 4.41 (d, *J* 17.4 Hz, 1H), 3.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 155.2, 131.4, 131.3, 130.8, 130.2, 130.1, 128.4, 127.4, 127.0, 125.0, 123.2, 121.6, 70.3, 52.1, 44.7; FTIR (film) *v*: 3421, 3343, 3024, 2950, 2842, 1715, 1508, 1227, 1068, 1037, 753 cm^{-1}: HRMS (ESI-TOF) *m*/*z* calcd for $C_{16}H_{15}NO_3Na$ [M + Na$^+$] 292.0950; Found 292.0941.

***t*-Butyl (2,5-Dihydrobenzo[*b*]oxepin-5-yl)carbamate (25o).** Yield 34 mg (75%) starting from 50 mg of carbamate **24o**; colorless oil; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.54 (d, *J* 8.7 Hz, 1H), 7.24−7.03 (m, 4H), 5.78−5.63 (m, 2H), 5.41 (dq, *J* 11.6, 2.5 Hz, 1H), 4.71 (dq, *J* 17.4, 2.8 Hz, 1H), 4.28 (dq, *J* 17.4, 2.6 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.2, 154.9, 137.0, 129.3, 129.1, 128.2, 127.8, 124.7, 121.8, 79.5, 70.9, 50.8, 28.4; FTIR (film) *v*: 3345, 2977, 2930, 1712, 1489, 1169 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_3Na$ [M + Na$^+$] 284.1263; Found 284.1265.

Benzyl (2,5-Dihydrobenzo[*b*]oxepin-5-yl)carbamate (25p). Yield 39 mg (85%) starting from 50 mg of compound **24p**; off-white solid, mp 106−108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38−7.23 (m, 7H), 7.14−7.05 (m, 2H), 6.07−5.99 (m, 1H), 5.68 (br d, *J* 9.1 Hz, 1H), 5.57 (br d, *J* 11.5 Hz, 1H), 5.34−5.26 (m, 1H), 5.13 (d, *J* 12.1 Hz, 1H), 5.03 (d, *J* 12.2 Hz, 1H), 4.69 (br d, *J* 17.4 Hz, 1H), 4.43 (br d, *J* 17.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 155.6, 136.6, 130.0, 129.5, 128.6(×2), 128.3, 128.2, 128.0, 127.8, 124.9, 122.0, 71.1, 67.0, 51.5; FTIR (film) *v*: 3330, 3031, 2936, 2843, 1713, 1491, 1262, 1227, 1041, 1026, 758, 697 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{17}NO_3Na$ [M + Na$^+$] 318.1106; Found 318.1107.

***N*-(2,5-Dihydrobenzo[*b*]oxepin-5-yl)acetamide (25q).** Yield 34 mg (77%) starting from 50 mg of carbamate **24q**; white solid, mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29−7.23 (m, 2H), 7.08 (ddt, *J* 7.4, 3.8, 1.9 Hz, 2H), 6.09−5.98 (m, 1H), 5.59 (ddd, *J* 11.6, 3.6, 1.9 Hz, 1H), 5.56−5.50 (m, 1H), 4.77−4.71 (m, 1H), 4.44−4.37 (m, 1H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.6, 157.4, 136.3, 129.9, 129.4, 128.5, 127.5, 124.9, 121.8, 71.0, 49.3, 23.4; FTIR (film) *v*: 3279, 3030, 2929, 2844, 1648, 1536, 1487, 1227, 1068, 758, 679 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{13}NO_2Na$ [M + Na$^+$] 226.0844; Found 226.0843.

***N*-(2,5-Dihydrobenzo[*b*]oxepin-5-yl)benzamide (25r).** Yield 38 mg (84%) starting from 50 mg of carbamate **24r**; white solid mp 155−156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* 7.2 Hz, 2H), 7.49−7.03 (m, 8H), 6.20−6.11 (m, 1H), 5.75 (t, *J* 8.2 Hz, 1H), 5.68−5.61 (m, 1H), 4.79 (br d, *J* 17.5 Hz, 1H), 4.45 (br d, *J* 17.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 157.5, 136.4, 134.4, 131.4, 130.2, 129.4, 128.5, 128.5, 127.6, 127.1, 124.9, 121.9, 71.1, 49.8; FTIR (film) v: 3310, 3060, 3030, 1640, 1533, 1485, 1224, 707, 697 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}NO_2Na$ [M + Na$^+$] 288.1000; Found 288.1002.

1-Benzyl-3-(2,5-dihydrobenzo[*b*]oxepin-5-yl)urea (25s). Yield 33 mg (72%) starting from 50 mg of carbamate **24s**; white solid, mp 161−162 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.29−7.01 (m, 9H), 6.14 (s, 2H), 5.87 (ddt, J 11.6, 5.5, 2.3 Hz, 1H), 5.77−5.71 (m, 1H), 5.51 (dtd, J 11.6, 2.8, 1.5 Hz, 1H), 4.53−4.50 (m, 2H), 4.39−4.26 (m, 2H); ^{13}C NMR (101 MHz, acetone-d_6) δ: 157.3, 140.7, 138.7, 129.8, 128.4, 128.21, 128.19, 127.2, 126.6, 124.1, 121.5, 70.6, 49.4, 43.5; FTIR (film) *v*: 3310, 3062, 3028, 2926, 2842, 1623, 1562, 1487, 1224, 756, 698, 675 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}N_2O_2Na$ [M + Na$^+$] 317.1266; Found 317.1261.

***N*-(2,5-Dihydrobenzo[*b*]oxepin-5-yl)morpholine-4-carboxamide (25t).** Yield 40 mg (88%) starting from 50 mg of carbamate **24t**; white solid, mp 161−162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28 (td, *J* 7.1, 1.6 Hz, 1H), 7.24 (dd, *J* 7.7, 1.7 Hz, 1H), 7.11−7.05 (m, 2H), 6.11 (dq, *J* 11.5, 4.6, 2.4 Hz, 1H), 5.57 (ddd, *J* 11.5, 3.6, 1.9 Hz, 1H), 5.39 (d, *J* 5.7 Hz, 2H), 4.74 (ddd, *J* 17.4, 3.6, 2.0 Hz, 1H), 4.40 (dt, *J* 17.4, 2.2 Hz, 1H), 3.63 (t, *J* 4.9 Hz, 4H), 3.37−3.26 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 156.7, 137.1, 129.5, 129.2, 128.6, 128.4, 124.9, 121.7, 71.1, 66.4, 50.8, 43.9; FTIR (film) *v*: 3331, 3029, 2962, 2920, 2894, 2853, 1628, 1535, 1485, 1267, 1224, 1117, 758, 734 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{18}N_2O_3Na$ [M + Na$^+$] 297.1215; Found 297.1213.

2-Amino-3-methylbenzoic Acid. Pd/C (10 wt %, 0.15 g) was added to a solution of 3-methyl-2-nitrobenzoic acid (4.3 g, 23.7 mmol) in 120 mL of AcOEt, and the solution was saturated with hydrogen for 14 h at room temperature. The progress of the reduction was followed by TLC (Hexane/AcOEt 50:50 v/v). Then, the reaction mixture was filtered through a Celite pad and the solution was concentrated on a rotary evaporator to afford the desired amino acid (3.36 g, 94%) as a white solid. The product was used in the next step without further purification. mp 172−173 °C [Lit.[49] 170−172 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* 7.9 Hz, 1H), 7.04 (d, *J* 7.2 Hz, 1H), 6.51−6.36 (m, 1H), 4.20 (br s, 2H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.9, 148.9, 134.7, 129.6, 123.0, 115.6, 110.4, 17.0; FTIR (film) v: 3505, 3373, 1667, 1571, 1320, 1240, 738 cm^{-1}; MS (ESI) *m*/*z* 150.1 [M − H$^-$].

2-Amino-4-methylbenzoic Acid. Prepared in the same manner as 2-amino-3-methylbenzoic acid; yield 3.92 g (95%) starting from 4.95 g of 4-methyl-2-nitrobenzoic acid; white solid, mp 176−177 °C (Lit.[50] 177−179 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* 8.1 Hz, 1H), 6.45−6.29 (m, 2H), 4.40 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.8, 150.7, 145.1, 131.8, 117.8, 116.8, 108.4, 21.4; FTIR (film) *v*: 3476, 3368, 1653, 1621, 1589, 1546, 1496, 1420, 1313, 1239, 1160, 770 cm^{-1}; LRMS (ESI-TOF) *m*/*z* 152.3 [M + H$^+$], 174.2 [M + Na$^+$], 190.4 [M + K$^+$].

2-Amino-5-methylbenzoic Acid. Prepared in the same manner as 2-amino-3-methylbenzoic acid; yield 3.92 g (94%) starting from 5 g of 5-methyl-2-nitrobenzoic acid; white solid, mp 173−174 °C (Lit.[51]

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174−176 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.11−7.01 (m, 1H), 6.60−6.49 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.9, 148.4, 135.4, 131.5, 125.6, 116.9, 110.2, 20.1; FTIR (film) ν: 3422, 2950, 1671, 1301, 1241, 811, 672, 519 cm^{-1}; MS (ESI) m/z 174.1 [M + Na$^+$].

(2-Amino-3-methylphenyl)methanol. A solution of 2-amino-3-methylbenzoic acid (3.36 g, 22.3 mmol) in dry THF (100 mL) was cooled to −15 °C, and a 2 M soln. of $LiAlH_4$ (26.7 mmol, 13.3 mL) in THF was added slowly. After 1 h at −5 °C, the reaction mixture was allowed to warm to room temperature and left overnight. The progress of the reaction was followed by TLC (hexanes/AcOEt 50:50 v/v). Next, the reaction mixture was poured carefully into a 2 M soln. of NaOH, stirred for 30 min, and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed under reduced pressure to obtain the crude product (2.77 g, 91%). This was directly taken to the next step without further purification. Orange solid, mp 68−70 °C (Lit.[52] 69−70 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (d, J 7.4 Hz, 1H), 6.96−6.92 (m, 1H), 6.65 (t, J 7.5 Hz, 1H), 4.65 (s, 2H), 4.16 (br s, 2H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.2, 130.6, 127.1, 124.2, 122.7, 117.6, 64.5, 17.3; MS (ESI) m/z 138 [M + H$^+$].

(2-Amino-4-methylphenyl)methanol. Prepared in the same manner as (2-amino-3-methylphenyl)methanol; yield 2.31 g (73%) starting from 3.5 g of amino-4-methylbenzoic acid; white solid, mp 142−143 °C (Lit.[53] 138−139 °C); ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.89 (d, J 7.5 Hz, 1H), 6.50 (s, 1H), 6.39−6.35 (m, 1H), 4.57 (s, 2H), 4.52 (d, J 5.4 Hz, 2H), 3.86 (t, J 5.4 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, acetone-d_6) δ: 146.9, 137.5, 128.3, 122.8, 117.3, 115.7, 62.7, 20.4; MS (ESI) m/z 138 [M + H$^+$].

(2-Amino-5-methylphenyl)methanol. Prepared in the same manner as (2-amino-3-methylphenyl)methanol; yield 2.39 g (67%) starting from 3.9 g of 2-amino-5-methylbenzoic acid; off-white solid; mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.88−6.80 (m, 2H), 6.55 (d, J 7.8 Hz, 1H), 4.50 (s, 2H), 3.30 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 142.7, 129.7, 129.3, 127.8, 125.5, 116.4, 63.3, 20.1; MS (ESI) m/z 138 [M + H$^+$].

***N*-(2-(Hydroxymethyl)phenyl)-4-methylbenzenesulfonamide.** A solution of 2-aminobenzyl alcohol (79.6 mmol, 10.0 g) and pyridine (12.8 g, 13.1 mL, 161.8 mmol) in dry CH_2Cl_2 (200 mL) was treated dropwise with a solution of TsCl (18.2 g, 95.5 mmol) in dry CH_2Cl_2 (50 mL). The progress of the reaction was followed by TLC. After completion of the reaction, the reaction mixture was diluted with CH_2Cl_2 and washed with water and brine. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated to give a crude product. The product was purified by recrystallization from AcOEt. white solid, mp 148−150 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.33 (s, 1H), 7.56 (d, J 8.3 Hz, 2H), 7.38−7.30 (m, 3H), 7.13 (pd, J 7.4, 1.7 Hz, 2H), 6.93 (dd, J 7.5, 1.6 Hz, 1H), 5.25 (s, 1H), 4.38 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 143.6, 137.8, 134.2, 130.1, 127.9, 127.6, 127.1, 126.4, 125.2, 59.9, 21.1.

***N*-(2-(Hydroxymethyl)-6-methylphenyl)-4-methylbenzenesulfonamide.** Prepared in the same manner as *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide; yield 2.83 g (48%) starting from 2.77 g of (2-amino-3-methylphenyl)methanol; white solid, mp 143−144 °C [Lit.[54] 143−144 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58−7.53 (m, 2H), 7.24−7.07 (m, 5H), 6.98 (s, 1H), 4.37 (s, 2H), 2.78 (s, 1H), 2.41 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.9, 139.1, 137.4, 137.3, 132.8, 130.9, 129.7, 127.9, 127.8, 127.2, 62.7, 21.6, 18.4; FTIR (film) ν: 3482, 3262, 2925, 1323, 1157, 1092, 666, 578 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}NO_3SNa$ [M + Na$^+$] 314.0827; Found 314.0826.

***N*-(2-(Hydroxymethyl)-4-methylphenyl)-4-methylbenzenesulfonamide.** Prepared in the same manner as *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide; yield 2.34 g (59%) starting from 1.86 g of (2-amino-5-methylphenyl)methanol; white solid, mp 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65−7.57 (m, 3H), 7.24−7.18 (m, 4H), 7.03 (d, J 8.1 Hz, 1H), 6.92 (s, 1H), 4.33 (d, J 4.6 Hz, 2H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.7, 136.9, 135.6, 133.3, 132.6, 129.9, 129.6, 129.6, 127.1, 124.4, 63.6, 21.5, 20.8; FTIR (film) ν: 3460, 3102, 2929, 2875, 2806, 2737, 1316, 1155, 1030 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}NO_3SNa$ [M + Na$^+$] 314.0827; Found 314.0824.

***N*-(2-(Hydroxymethyl)-5-methylphenyl)-4-methylbenzenesulfonamide.** Prepared in the same manner as *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide; yield 3.92 (80%) starting from 2.32 g of (2-amino-4-methylphenyl)methanol; white solid, mp 135−136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.63 (d, J 8.3 Hz, 2H), 7.26 (s, 1H), 7.21 (d, J 8.0 Hz, 2H), 6.95 (d, J 7.7 Hz, 1H), 6.88 (d, J 7.6 Hz, 1H), 4.32 (d, J 5.5 Hz, 2H), 2.38 (s, 3H), 2.29 (s, 3H), 2.07 (t, J 5.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.7, 139.4, 137.0, 136.2, 129.6, 128.9, 128.8, 127.0, 126.1, 124.2, 63.6, 21.5, 21.2; FTIR (film) ν: 3463, 3254, 2945, 1325, 1164, 115, 1092, 817, 661, 569 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{17}NO_3SNa$ [M + Na$^+$] 314.0827; Found 314.0827.

***N*-(2-Formylphenyl)-4-methylbenzenesulfonamide (26a).** To a stirred suspension of PCC (16.4 g, 74.7 mmol) in dry CH_2Cl_2 (200 mL) was added dropwise a solution of *N*-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide (10.3 g, 37.3 mmol) in the same solvent (25 mL). The mixture was stirred at room temperature for 2−3 h (progress of the reaction followed by TLC). Next, the reaction mixture was diluted with Et_2O, stirred for 30 min, and filtered. The solid was washed several times with Et_2O. The combined organic layers were passed through a short pad of silica gel and evaporated to give the product. The crude product was recrystallized from AcOEt/hexanes to afford 6.91 g (67%) of aldehyde **26a** as a white solid. mp 138−139 °C (Lit.[55] 134−136 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.77 (s, 1H), 9.82 (d, J 0.6 Hz, 1H), 7.79−7.74 (m, 2H), 7.69 (d, J 8.4 Hz, 1H), 7.58 (dd, J 7.6, 1.6 Hz, 1H), 7.55−7.45 (m, 1H), 7.25−7.21 (m, 2H), 7.15 (td, J 7.5, 1.0 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.9, 144.1, 140.0, 136.4, 136.1, 135.8, 129.7, 127.3, 122.9, 121.9, 117.8, 21.5; FTIR (film) ν: 3438, 3141, 3067, 2980, 2856, 2767, 1668, 1601, 1583, 1495, 1458, 1408, 1341, 1292, 1203, 1158, 1090, 929, 843, 812, 761, 603, 565 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{13}NO_3SNa$ [M + Na$^+$] 298.0514; Found 298.0513.

***N*-(2-Formyl-6-methylphenyl)-4-methylbenzenesulfonamide (26b).** Prepared in the same manner as compound **26a**; yield 2.24 g (80%) starting from 2.83 g of *N*-(2-(hydroxymethyl)-6-methylphenyl)-4-methylbenzenesulfonamide; yellowish solid, mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.62 (s, 1H), 8.25 (s, 1H), 7.47 (d, J 7.5 Hz, 2H), 7.41−7.37 (m, 2H), 7.34−7.29 (m, 1H), 7.16−7.12 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 192.6, 144.1, 138.3, 137.5, 136.0, 135.7, 131.3, 131.2, 129.4, 127.6, 127.2, 21.6, 18.7; FTIR (film) ν: 3126, 1661, 1581, 1338, 1250, 1155, 1087, 774, 663, 577, 533 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}NO_3SNa$ [M + Na$^+$] 312.0670; Found 312.0667.

***N*-(2-Formyl-5-methylphenyl)-4-methylbenzenesulfonamide (26c).** Prepared in the same manner as compound **26a**; yield 2.99 g (77%) starting from 3.92 g of *N*-(2-(hydroxymethyl)-5-methylphenyl)-4-methylbenzenesulfonamide; white solid, mp 158−159 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.79 (s, 1H), 9.74 (s, 1H), 7.77−7.73 (m, 2H), 7.49 (s, 1H), 7.44 (d, J 7.8 Hz, 1H), 7.23 (d, J 7.8 Hz, 2H), 6.96−6.93 (m, 1H), 2.36 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 194.3, 147.6, 144.1, 140.0, 136.5, 136.1, 129.7, 127.2, 124.0, 119.9, 118.2, 22.4, 21.5; FTIR (film) ν: 3304, 3150, 2984, 2843, 2758, 1674, 1509, 1395, 1157, 887, 814, 660, 612, 567, 543 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}NO_3SNa$ [M + Na$^+$] 312.0670; Found 312.0666.

***N*-(2-Formyl-4-methylphenyl)-4-methylbenzenesulfonamide (26d).** Prepared in the same manner as compound **26a**; yield 1.9 g (82%) starting from 2.34 g of *N*-(2-(hydroxymethyl)-4-methylphenyl)-4-methylbenzenesulfonamide; white solid, mp 113−114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.57 (s, 1H), 9.76 (s, 1H), 7.75−7.70 (m, 2H), 7.59 (d, J 8.5 Hz, 1H), 7.35 (s, 1H), 7.30 (dd, J 8.5, 1.9 Hz, 1H), 7.21 (d, J 8.1 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.0, 144.0, 137.4, 136.6, 136.5, 136.2, 132.9, 129.7, 127.2, 122.1, 118.2, 21.5, 20.3; FTIR (film) ν: 3185, 2925, 2856, 166, 1496, 1403, 1342, 1168, 1151, 1091, 899, 770, 679, 581, 546 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}NO_3SNa$ [M + Na$^+$] 312.0670; Found 312.0675.

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***N*-Allyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide (27a).** A solution of *N*-Ts-amino benzaldehyde **26a** (6.9 g, 25.1 mmol) in dry DMF (25 mL) was added to a stirred suspension of NaH (60% disp. in oil, 1.21 g, 30.1 mmol) in dry DMF (125 mL) at 0 °C. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h. Allyl bromide (4.54 g, 3.2 mL, 37.5 mmol) was added dropwise, and the mixture was stirred until complete consumption of the starting material (TLC). The reaction mixture was diluted with water and extracted with Et_2O. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was recrystallized from AcOEt/hexanes mixture to afford 5.94 g (75%) as a white solid. mp 110−111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.37 (s, 1H), 8.02−7.92 (m, 1H), 7.49−7.39 (m, 4H), 7.29−7.26 (m, 2H), 6.76−6.68 (m, 1H), 5.73 (ddt, *J* 16.9, 10.1, 6.8 Hz, 1H), 5.08−4.93 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.1, 144.2, 141.3, 136.0, 134.5, 134.0, 131.6, 129.7, 128.6, 128.4, 128.0, 127.9, 120.4, 54.4, 21.6; FTIR (film) *v*: 3070, 3033, 2981, 2924, 2862, 2751, 1696, 1596, 1482, 1455, 1350, 1166, 1091, 1056, 864, 822, 727, 664, 578, 548 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{17}NO_3SNa$ [M + Na$^+$] 338.0827; Found 338.0820.

***N*-Allyl-*N*-(2-formyl-6-methylphenyl)-4-methylbenzenesulfonamide (27b).** Prepared in the same manner as compound **27a**; yield 3.33 g (79%) starting from 3.69 g of compound **26b**; yellowish solid, mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.80 (d, *J* 0.6 Hz, 1H), 7.78 (dd, *J* 7.6, 1.3 Hz, 1H), 7.57 (d, *J* 8.3 Hz, 1H), 7.47−7.44 (m, 1H), 7.36 (t, *J* 7.6 Hz, 1H), 7.28 (d, *J* 8.3 Hz, 2H), 5.90−5.80 (m, 1H), 5.07 (d, *J* 10.0 Hz, 1H), 5.00 (dq, *J* 17.0, 1.2 Hz, 1H), 4.40 (dd, *J* 14.4, 6.5 Hz, 1H), 4.00 (dd, *J* 14.5, 7.7 Hz, 1H), 2.43 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.5, 144.0, 139.8, 139.5, 137.2, 136.9, 136.0, 132.0, 129.9(×2), 128.8, 127.2(×2), 126.6, 120.5, 54.9, 21.6, 18.1; FTIR (film) *v*: 3066, 3016, 2980, 2925, 2876, 2755, 1688, 1585, 1348, 1243, 1162, 1092, 1064, 863, 730, 663, 586, 538 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}NO_3SNa$ [M + Na$^+$] 352.0983; Found 352.0974.

***N*-Allyl-*N*-(2-formyl-5-methylphenyl)-4-methylbenzenesulfonamide (27c).** Prepared in the same manner as compound **27a**; yield 2 g (62%) starting from 2.9 g of compound **26c**; yellowish soild, mp 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.26 (s, 1H), 7.85 (d, *J* 7.9 Hz, 1H), 7.51−7.48 (m, 2H), 7.30−7.26 (m, 2H), 7.22 (d, *J* 7.9 Hz, 1H), 6.52 (s, 1H), 5.73 (ddt, *J* 16.9, 10.1, 6.7 Hz, 1H), 5.07−4.99 (m, 2H), 2.44 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.9, 145.3, 144.1, 141.4, 134.7, 133.5, 131.8, 129.6, 129.5, 128.8, 128.3, 127.9, 120.2, 54.5, 21.59, 21.56; FTIR (film) *v*: 3032, 2981, 2924, 2864, 2754, 1691, 1351, 1165, 1091, 833, 711, 665, 578, 547 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}NO_3SNa$ [M + Na$^+$] 352.0983; Found 352.0984.

***N*-Allyl-N-(2-formyl-4-methylphenyl)-4-methylbenzenesulfonamide (27d).** Prepared in the same manner as compound **27a**; yellow oil; yield 1.36 g (85%) starting from 1.39 g of compound **26d**; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.34 (s, 1H), 7.77 (d, *J* 1.8 Hz, 1H), 7.52−7.47 (m, 2H), 7.30−7.24 (m, 3H), 6.61 (d, *J* 8.1 Hz, 1H), 5.73 (ddt, *J* 16.9, 10.1, 6.8 Hz, 1H), 5.06−4.97 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.4, 144.1, 138.84, 138.78, 135.6, 134.8, 134.7, 131.7, 129.6, 128.7, 127.92, 127.88, 120.3, 54.5, 21.6, 21.0; FTIR (film) *v*: 3031, 2954, 2925, 2857, 1690, 1604, 1493, 1350, 1164, 1091, 860, 664, 563 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}NO_3S$ [M + Na$^+$] 352.0983; Found 352.0985.

Ethyl (*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-phenyl)acrylate (28a). Prepared in the same manner as compound **19a**; yield 4.93 g (68%) starting from 5.94 g of aldehyde **27a**; white solid, mp 139−140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* 16.1 Hz, 1H), 7.63 (dd, *J* 7.6, 1.8 Hz, 1H), 7.59−7.55 (m, 2H), 7.35−7.23 (m, 4H), 6.90 (dd, *J* 7.7, 1.4 Hz, 1H), 6.31 (d, *J* 16.1 Hz, 1H), 5.76 (ddt, *J* 16.9, 10.1, 6.7 Hz, 1H), 5.03−4.94 (m, 2H), 4.25 (q, *J* 7.1 Hz, 2H), 2.42 (s, 3H), 1.34 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.3, 143.8, 140.1, 138.3, 135.6, 135.5, 132.1, 130.3, 129.8, 129.6, 128.7, 127.9, 127.0, 120.0, 119.6, 60.3, 54.8, 21.4, 14.3; FTIR (film) *v*: 3066, 3030, 2981, 2926, 2871, 1712, 1635, 1484, 1451, 1351, 1316, 1270, 1165, 1092, 1043, 862, 767, 663, 573, 552 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{23}NO_4SNa$ [M + Na$^+$] 408.1245; Found 408.1241.

Ethyl (*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-3-methylphenyl)acrylate (28b). Prepared in the same manner as compound **19a**; yield 3.05 g (75%) starting from 3.33 g of aldehyde **27b**; white solid, mp 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* 8.3 Hz, 2H), 7.42 (d, *J* 7.6 Hz, 1H), 7.31−7.20 (m, 5H), 6.15 (d, *J* 15.9 Hz, 1H), 5.85 (ddt, *J* 16.9, 10.0, 7.2 Hz, 1H), 5.05−4.97 (m, 2H), 4.28−4.03 (m, 4H), 2.40 (s, 3H), 2.35 (s, 3H), 1.27 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 143.5, 141.2, 140.9, 137.5, 137.2, 135.0, 133.2, 132.5, 129.7, 128.7, 127.5, 124.7, 119.7, 119.6, 60.2, 54.8, 21.5, 19.4, 14.2; FTIR (film) *v*: 3067, 2981, 2927, 2871, 1712, 1633, 1461, 1348, 1311, 1182, 1163, 1092, 1040, 864, 663, 574, 544 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{25}NO_4SNa$ [M + Na$^+$] 422.1402; Found 422.1403.

Ethyl (*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-4-methylphenyl)acrylate (28c). Prepared in the same manner as compound **19a**; yield 910 mg (76%) starting from 978 mg of aldehyde **27c**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* 16.1 Hz, 1H), 7.60−7.56 (m, 2H), 7.51 (d, *J* 8.0 Hz, 1H), 7.26 (d, *J* 8.0 Hz, 2H), 7.15−7.10 (m, 1H), 6.76−6.72 (m, 1H), 6.25 (d, *J* 16.1 Hz, 1H), 5.75 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.05−4.94 (m, 2H), 4.23 (q, *J* 7.1 Hz, 2H), 2.41 (s, 3H), 2.27 (s, 3H), 1.32 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 143.7, 140.9, 139.9, 138.2, 135.8, 132.5, 132.3, 130.8, 129.7, 129.5, 128.0, 126.8, 119.5, 119.1, 60.3, 54.9, 21.5, 21.2, 14.3; FTIR (film) *v*: 3067, 3029, 2981, 2925, 2871, 1713, 1634, 1352, 1316, 1268, 1164, 1091, 817, 664, 587, 559 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{25}NO_4SNa$ [M + Na$^+$] 422.1402; Found 422.1399.

Ethyl (*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-5-methylphenyl)acrylate (28d). Prepared in the same manner as compound **19a**; yield 1.37 g (61%) starting from 1.86 g of aldehyde **27d**; off-white solid, mp 87−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, *J* 16.1 Hz, 1H), 7.57 (d, *J* 8.3 Hz, 2H), 7.43 (s, 1H), 7.25 (d, *J* 8.3 Hz, 2H), 7.08 (dd, *J* 8.1, 1.7 Hz, 1H), 6.77 (d, *J* 8.1 Hz, 1H), 6.29 (d, *J* 16.1 Hz, 1H), 5.75 (ddt, *J* 16.9, 10.1, 6.7 Hz, 1H), 5.03−4.94 (m, 2H), 4.24 (q, *J* 7.1 Hz, 2H), 2.41 (s, 3H), 2.34 (s, 3H), 1.33 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 143.6, 140.2, 138.6, 135.8, 135.7, 135.2, 132.3, 131.2, 129.8, 129.5, 128.0, 127.6, 119.9, 119.5, 60.4, 54.9, 21.5, 21.2, 14.3; FTIR (film) *v*: 3067, 3029, 2981, 2925, 2870, 1713, 1636, 1493, 1351, 1317, 1266, 1165, 1091, 858, 664, 557 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{25}NO_4SNa$ [M + Na$^+$] 422.1402; Found 422.1405.

(*E*)-*N*-Allyl-*N*-(2-(3-hydroxyprop-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (29a). Prepared in the same manner as compound **20a**; yield 3.51 g (80%) starting from 4.93 g of ester **28a**; colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63−7.55 (m, 1H), 7.31−7.24 (m, 3H), 7.12 (td, *J* 7.9, 1.3 Hz, 1H), 6.82 (d, *J* 16.0 Hz, 1H), 6.71 (dd, *J* 8.1, 1.0 Hz, 1H), 6.32 (dt, *J* 16.0, 5.8 Hz, 1H), 5.73 (ddt, *J* 16.9, 10.1, 6.7 Hz, 1H), 5.02−4.90 (m, 2H), 4.28−4.24 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 143.5, 137.7, 136.6, 136.2, 132.3, 130.7, 129.4, 129.4, 128.5, 128.3, 127.9, 127.8, 126.6, 126.4, 119.3, 63.7, 54.8, 21.5; IR (film) *v*: 3504, 3407, 3065, 3029, 2981, 2922, 2863, 1598, 1483, 1450, 1345, 1164, 1091, 722, 664, 577 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{21}NO_3SNa$ [M + Na$^+$] 366.1140; Found 366.1140.

(*E*)-*N*-Allyl-*N*-(2-(3-hydroxyprop-1-en-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (29b). Prepared in the same manner as compound **20a**; yield 2.13 g (58%) starting from 4.09 g of ester **28b**; white solid, mp 102−103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70−7.66 (m, 2H), 7.35 (dd, *J* 7.4, 1.8 Hz, 1H), 7.30−7.27 (m, 2H), 7.20−7.12 (m, 2H), 6.16 (dt, *J* 15.8, 5.0 Hz, 1H), 6.09 (br d, *J* 15.8 Hz, 1H), 5.90−5.78 (m, 1H), 5.02−4.96 (m, 2H), 4.24 (ddt, *J* 14.4, 6.5, 1.1 Hz, 1H), 4.01−3.94 (m, 3H), 2.43 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.4, 140.4, 138.0, 136.8, 135.9, 132.7, 130.7, 130.4, 129.5, 128.5, 127.7, 127.2, 124.0, 119.3, 63.6, 54.5, 21.5, 19.4; FTIR (film) *v*: 3524, 3064, 3027, 2979, 2924, 285, 1455, 1160, 1091 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{23}NO_3SNa$ [M + Na$^+$] 380.1296; Found 380.1306.

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(*E*)-*N*-Allyl-*N*-(2-(3-hydroxyprop-1-en-1-yl)-5-methylphenyl)-4-methylbenzenesulfonamide (29c). Prepared in the same manner as compound **20a**; yield 543 mg (67%) starting from 910 mg of ester **28c**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* 8.3 Hz, 2H), 7.47 (d, *J* 8.0 Hz, 1H), 7.28 (d, *J* 8.3 Hz, 2H), 7.07 (d, *J* 8.0 Hz, 1H), 6.70 (d, *J* 16.0 Hz, 1H), 6.54−6.52 (m, 1H), 6.26 (dt, *J* 16.0, 5.8 Hz, 1H), 5.73 (ddt, *J* 16.9, 10.3, 6.7 Hz, 1H), 5.02−4.95 (m, 2H), 4.22 (t, J 5.3 Hz, 2H), 4.19−3.98 (m, 2H), 2.44 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.5, 137.9, 136.5, 136.3, 134.6, 132.5, 130.1, 129.6, 129.5, 129.4, 127.9, 126.7, 126.2, 119.1, 63.9, 54.8, 21.5, 20.9; FTIR (film) *v*: 3507, 3029, 2922, 2863, 1497, 1346, 1162, 1095, 815, 713, 663, 549 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{23}NO_3S$ [M + Na$^+$] 380.1296; Found 380.1296.

(*E*)-*N*-Allyl-*N*-(2-(3-hydroxyprop-1-en-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (29d). Prepared in the same manner as compound **20a**; yield 817 mg (66%) starting from 1.37 g of ester **28d**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.62−7.54 (m, 2H), 7.40 (d, J 1.6 Hz, 2H), 7.29−7.26 (m, 2H), 6.93 (dd, *J* 8.1, 1.7 Hz, 1H), 6.78 (dt, *J* 16.0, 1.4 Hz, 2H), 6.58 (d, *J* 8.1 Hz, 1H), 6.31 (dt, *J* 16.0, 5.8 Hz, 1H), 5.72 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.01−4.94 (m, 3H), 4.27−4.17 (m, 3H), 4.03−3.96 (m, 1H), 2.43 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.4, 138.4, 137.2, 136.3, 134.1, 132.5, 130.4, 129.4, 129.1, 128.3, 127.9, 127.0, 126.8, 119.2, 63.8, 54.8, 21.5, 21.2; FTIR (film) *v*: 3500, 3027, 2922, 2862, 1598, 1492, 1345, 1162, 1091, 861, 665, 553 cm^{-1}; HRMS (ESI-TOF) *m*/*z* cald for $C_{20}H_{23}NO_3S$ [M + Na$^+$] 380.1296; Found 380.1292.

(*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)phenyl)allyl Carbamate (30a). Prepared in the same manner as compound **21a**; yield 3.19 g (81%) starting from 3.5 g of allyl alcohol **29a**; white solid, mp 116−118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (m, 3H), 7.26 (m, 3H), 7.17−7.08 (m, 1H), 6.85 (d, *J* 16.0 Hz, 1H), 6.72 (d, *J* 7.9 Hz, 1H), 6.22 (dt, *J* 16.0, 6.2 Hz, 1H), 5.71 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.00−4.86 (m, 4H), 4.68−4.61 (m, 2H), 4.19 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.7, 143.6, 137.3, 136.8, 136.1, 132.3, 129.5, 129.4, 129.1, 128.6, 128.2, 127.9, 126.5, 125.7, 119.4, 65.5, 54.8, 21.5; FTIR (film) *v*: 3485, 3375, 3197, 304, 2975, 1725, 1598, 1400, 1338, 1164, 1092, 1055, 664, 577 cm^{-1}; HRMS (ESI-TOF) *m*/*z* $C_{20}H_{22}N_2O_4SNa$ [M + Na$^+$] 409.1198; Found 409.1201.

(*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-3-methylphenyl)allyl Carbamate (30b). Prepared in the same manner as compound **21a**; yield 1.95 g (85%) starting from 2.0 g of allyl alcohol **29b**; white solid, mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* 8.3 Hz, 2H), 7.36 (dd, *J* 7.0, 2.3 Hz, 1H), 7.28 (d, *J* 8.3 Hz, 2H), 7.21−7.14 (m, 2H), 6.16 (d, *J* 15.8 Hz, 1H), 6.08 (dt, *J* 15.8, 5.6 Hz, 1H), 5.87−5.76 (m, 1H), 5.02−4.95 (m, 2H), 4.75 (br s, 2H), 4.41−4.31 (m, 2H), 4.21 (dd, *J* 14.4, 6.5 Hz, 1H), 3.97 (dd, *J* 14.4, 7.5 Hz, 1H), 2.43 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 143.5, 140.4, 137.9, 136.4, 136.1, 132.6, 131.0, 130.0, 129.6, 128.4, 127.6, 125.2, 124.0, 119.3, 65.6, 54.4, 21.5, 19.4; FTIR (film) v: 3476, 3376, 3196, 3065, 3027, 2926, 1723, 1598, 1399, 1336, 1160, 1053, 665, 582 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{24}N_2O_4$-SNa [M + Na$^+$] 423.1831; Found 423.1842.

(*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-4-methylphenyl)allyl Carbamate (30c). Prepared in the same manner as compound **21a**; yield 500 mg (82%) starting from 543 mg of allyl alcohol **29c**; white solid, mp 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, *J* 8.3 Hz, 2H), 7.46 (d, *J* 8.0 Hz, 1H), 7.28 (d, *J* 8.3 Hz, 2H), 7.07 (d, *J* 8.0 Hz, 1H), 6.75 (d, *J* 16.0 Hz, 1H), 6.57−6.55 (m, 1H), 6.17 (dt, *J* 16.0, 6.2 Hz, 1H), 5.72 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.02−4.94 (m, 2H), 4.72 (s, 2H), 4.64−4.61 (m, 2H), 4.19−4.12 (m, 1H), 4.05−3.96 (m, 1H), 2.44 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 143.5, 138.3, 136.7, 136.3, 134.1, 132.5, 130.2, 129.5, 129.4, 129.1, 127.9, 126.2, 124.6, 119.1, 65.7, 54.7, 21.5, 20.9; FTIR (film) *v*: 3477, 3376, 3196, 3029, 2923, 1725, 1337, 1162, 1092, 1052 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{24}N_2O_4SNa$ [M + Na$^+$] 423.1354; Found 423.1355.

(*E*)-3-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-5-methylphenyl)allyl Carbamate (30d). Prepared in the same manner as compound **21a**; yield 657 mg (72%) starting from 817 mg of allyl alcohol **29d**; white solid, mp 142−143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 (d, *J* 8.3 Hz, 2H), 7.39 (d, *J* 1.5 Hz, 1H), 7.27 (d, *J* 8.3 Hz, 2H), 6.94 (dd, *J* 8.1, 1.6 Hz, 1H), 6.83 (br d, *J* 16.0 Hz, 1H), 6.60 (d, *J* 8.1 Hz, 1H), 6.22 (dt, *J* 16.0, 6.2 Hz, 1H), 5.71 (ddt, *J* 16.9, 10.2, 6.7 Hz, 1H), 5.01−4.93 (m, 2H), 4.75 (s, 2H), 4.67−4.63 (m, 2H), 4.28−4.15 (m, 1H), 4.06−3.92 (m, 1H), 2.43 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 143.5, 138.4, 136.8, 136.3, 134.3, 132.5, 129.5, 129.3, 129.1, 129.0, 127.9, 127.0, 125.3, 119.2, 65.6, 54.8, 21.5, 21.2; FTIR (film) *v*: 3482, 3377, 3196, 3029, 2979, 2924, 1726, 1598, 1498, 1400, 1347, 1162, 1092, 1054, 664 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{24}N_2O_4SNa$ [M + Na$^+$] 423.1354; Found 423.1352.

Methyl (1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)phenyl)-allyl)carbamate (31a). Prepared in the same manner as compound **24a**; yield 134 mg (86%) starting from 150 mg of carbamate **30a**; white solid, mp 117−118 °C; ^{1}H NMR (500 MHz, DMSO-d_6, mixture of rotamers (3:1), data for major rotamer) δ: 7.69 (d, *J* 9.5 Hz, 1H), 7.56 (d, *J* 8.3 Hz, 2H), 7.41 (d, *J* 8.3 Hz, 2H), 7.40−7.38 (m, 1H), 7.30 (td, *J* 7.6, 1.1 Hz, 1H), 7.17−7.13 (m, 1H), 6.55 (d, *J* 8.0 Hz, 1H), 5.94 (ddd, *J* 17.3, 10.5, 4.0 Hz, 1H), 5.81−5.77 (m, 1H), 5.72−5.63 (m, 1H), 5.23 (d, *J* 17.4 Hz, 1H), 5.11 (d, *J* 10.5 Hz, 1H), 4.94−4.86 (m, 2H), 4.34 (dd, *J* 14.5, 5.8 Hz, 1H), 3.95 (dd, *J* 14.5, 7.7 Hz, 1H), 3.52 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ: 156.4, 144.2, 142.8, 138.9, 136.6, 135.7, 133.0, 130.2, 129.7, 129.1, 128.6, 128.2, 128.1, 119.7, 113.6, 54.8, 51.9, 51.1, 21.5; FTIR (film) *v*: 3377, 3064, 3028, 2982, 2952, 2924, 1723, 1521, 1347, 1237, 1163, 1090, 663, 580, 550 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{24}N_2O_4SNa$ [M + Na$^+$] 423.1354; Found 423.1363.

Methyl (1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-3-methylphenyl)allyl)carbamate (31b). Prepared in the same manner as compound **24a**; yield 128 mg (82%) starting from 150 mg of allyl carbamate **30b**; white solid, mp 105−106 °C; ^{1}H NMR (600 MHz, DMSO-d_6, 90 °C) δ: 7.70−7.65 (m, 2H), 7.40−7.38 (m, 2H), 7.23−7.19 (m, 2H), 7.14−7.11 (m, 1H), 7.05 (s, 1H), 5.83 (ddd, *J* 17.3, 10.5, 3.9 Hz, 1H), 5.73 (ddt, *J* 17.0, 10.0, 6.9 Hz, 1H), 5.43−5.39 (m, 1H), 5.11 (dt, *J* 17.3, 1.7 Hz, 1H), 5.06 (dt, *J* 10.5, 1.8 Hz, 1H), 4.95 (dq, *J* 17.0, 1.3 Hz, 1H), 4.92−4.89 (m, 1H), 4.21 (dd, *J* 14.7, 6.9 Hz, 1H), 4.17 (dd, *J* 14.7, 7.0 Hz, 1H), 3.51 (s, 3H), 2.40 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6, 90 °C) δ: 156.2, 143.9, 142.5, 139.5, 139.2, 138.0, 136.0, 133.2, 130.7, 130.1, 128.8, 127.8, 127.7, 119.1, 113.6, 54.2, 52.3, 51.7, 21.3, 19.5; FTIR (film) *v*: 3375, 3083, 3064, 3020, 2983, 2953, 2926, 1723, 1520, 1343, 1241, 1161, 1090, 737, 664 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{26}N_2O_4SNa$ [M + Na$^+$] 437.1511; Found 437.1512.

Methyl (1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-5-methylphenyl)allyl)carbamate (31c). Prepared in the same manner as compound **24a**; yield 130 mg (84%) starting from 150 mg of carbamate **30c**; white solid, mp 124−126 °C; ^{1}H NMR (400 MHz, DMSO-d_6, mixture of rotamers (ratio 4.8:1), data for major rotamer) δ: 7.59 (d, *J* 8.6 Hz, 1H), 7.57−7.53 (m, 2H), 7.43−7.38 (m, 2H), 7.18 (d, *J* 1.6 Hz, 1H), 6.94 (dd, *J* 8.2, 1.6 Hz, 1H), 6.42 (d, *J* 8.1 Hz, 1H), 5.92 (ddd, *J* 17.3, 10.5, 3.9 Hz, 1H), 5.76−5.71 (m, 1H), 5.70−5.62 (m, 1H), 5.22 (d, *J* 17.3 Hz, 1H), 5.10 (d, *J* 10.5 Hz, 1H), 4.95−4.85 (m, 2H), 4.31 (dd, *J* 14.5, 5.7 Hz, 1H), 3.92 (dd, *J* 14.5, 7.7 Hz, 1H), 3.52 (s, 3H), 2.40 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6, mixture of rotamers, data for major rotamer) δ: 156.4, 144.1, 142.4, 139.9, 139.0, 138.5, 135.8, 134.2, 133.9, 133.1, 130.2, 128.8, 128.2, 119.6, 113.4, 54.8, 51.9, 51.0, 21.5, 21.2; FTIR (film) v: 3377, 3083, 3024, 2983, 2953, 2924, 1725, 1521, 1500, 1348, 1238, 1163, 1090, 861, 664, 555 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{26}N_2O_4SNa$ [M + Na$^+$] 437.1511; Found 437.1502.

Methyl (1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-4-methylphenyl)allyl)carbamate (31d). Prepared in the same manner as compound **24a**; yield 129 mg (83%) starting from 150 mg of carbamate **30d**; white solid, mp 130−131 °C; ^{1}H NMR (600 MHz, DMSO-d_6, mixture of rotamers (2.3:1), data for major rotamer) δ: 7.62 (d, *J* 9.5 Hz, 1H), 7.54 (d, *J* 8.2 Hz, 2H), 7.41 (d, *J* 8.2 Hz, 2H), 7.24 (d, *J* 8.0 Hz, 1H), 7.11 (d, *J* 8.0 Hz, 1H), 6.32 (s, 1H), 5.88 (ddd, *J* 17.3, 10.5, 4.0 Hz, 1H), 5.71−5.63 (m, 2H), 5.18 (d, *J* 17.3 Hz, 1H), 5.07 (d, *J* 10.5 Hz, 1H), 4.92 (d, *J* 17.1 Hz, 1H), 4.87 (d, *J* 10.1

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Hz, 1H), 4.29 (dd, *J* 14.5, 5.5 Hz, 1H), 3.90 (dd, *J* 14.5, 7.6 Hz, 1H), 3.50 (s, 3H), 2.40 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ: 156.4, 144.2, 139.6, 139.1, 137.5, 136.4, 135.7, 133.1, 130.1, 129.8, 129.5, 129.0, 128.3, 119.6, 113.3, 54.7, 51.8, 50.9, 21.5, 20.8; FTIR (film) *v*: 3377, 3083, 3025, 2983, 2952, 2924, 1723, 1504, 1349, 1162, 1089, 663, 580, 551 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{26}N_2O_4SNa$ [M + Na$^+$] 437.1511; Found 437.1502.

***t*-Butyl (1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)phenyl)-allyl)carbamate (31e).** Prepared in the same manner as compound **24o**; yield 169 mg (90%) starting from 150 mg of carbamate **30a**; white solid, mp 86−87 °C; ^{1}H NMR (400 MHz, DMSO-d_6, mixture of rotamers, data for major rotamer) δ: 7.55 (d, *J* 8.3 Hz, 2H), 7.41 (d, *J* 8.3 Hz, 2H), 7.33−7.24 (m, 2H), 7.17−7.10 (m, 2H), 6.53 (d, *J* 8.0 Hz, 0H), 5.91 (ddd, *J* 17.3, 10.4, 4.0 Hz, 1H), 5.84−5.68 (m, 2H), 5.23 (dt, *J* 17.3, 1.9 Hz, 1H), 5.09 (dt, *J* 10.4, 1.9 Hz, 1H), 4.95−4.81 (m, 2H), 4.38 (dd, *J* 14.4, 5.5 Hz, 1H), 3.91 (dd, *J* 14.4, 7.9 Hz, 1H), 2.40 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6, mixture of rotamers, data for major rotamer) δ: 155.2, 144.1, 143.1, 139.3, 136.3, 135.7, 133.2, 130.2, 130.0, 129.0, 128.7, 128.2, 128.0, 119.5, 113.3, 78.4, 54.7, 50.5, 28.6, 21.5; FTIR (film) v: 3366, 3083, 3055, 2978, 2929, 1708, 1492, 1352, 1165, 1092, 860, 665, 590, 550 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{30}N_2O_4SNa$ [M + Na$^+$] 465.1824; Found 465.1831.

***N*-(1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)phenyl)allyl)-acetamide (31f).** Prepared in the same manner as compound **24q**; yield 105 mg (70%) starting from 150 mg of carbamate **30a**; off-white solid, mp 170−172 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.11 (d, *J* 8.8 Hz, 1H), 7.56 (d, *J* 8.0 Hz, 2H), 7.41 (d, *J* 8.0 Hz, 2H), 7.38−7.31 (m, 2H), 7.19−7.13 (m, 1H), 6.57 (d, *J* 7.9 Hz, 1H), 6.05−6.00 (m, 1H), 5.89 (ddd, *J* 17.2, 10.5, 3.9 Hz, 1H), 5.71−5.58 (m, 1H), 5.18 (dt, *J* 17.2, 1.9 Hz, 1H), 5.10 (dt, *J* 10.5, 1.9 Hz, 1H), 4.93−4.85 (m, 2H), 4.33 (dd, *J* 14.5, 5.8 Hz, 1H), 3.94 (dd, *J* 14.5, 7.7 Hz, 1H), 2.40 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 168.6, 144.1, 142.7, 139.0, 136.7, 135.9, 133.1, 130.2, 129.8, 129.1, 128.7, 128.2, 128.1, 119.5, 113.5, 54.7, 49.0, 23.0, 21.5; FTIR (film) *v*: 3377, 3290, 3063, 3031, 2979, 2925, 1656, 1536, 1346, 1163, 1092, 737, 664, 579, 550 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{21}H_{24}N_2O_3S$ [M + Na$^+$] 407.1403; Found 407.1407.

***N*-Allyl-*N*-(2-(1-(3-butylureido)allyl)phenyl)-4-methyl-benzenesulfonamide (31g).** Prepared in the same manner as compound **24s**; yield 145 mg (85%) starting from 150 mg of compound **30a**; white solid, mp 156−157 °C; ^{1}H NMR (400 MHz, DMSO-d_6, mixture of rotamers, data for main rotamer) δ: 7.56 (d, *J* 8.0 Hz, 2H), 7.41 (d, *J* 8.0 Hz, 2H), 7.36−7.30 (m, 1H), 7.20 (dd, *J* 7.8, 1.6 Hz, 1H), 7.17−7.12 (m, 1H), 6.59 (dd, *J* 8.0, 1.3 Hz, 1H), 6.15 (d, *J* 8.9 Hz, 1H), 5.90 (ddd, *J* 17.3, 10.4, 3.6 Hz, 1H), 5.83−5.64 (m, 2H), 5.18 (dt, *J* 17.3, 1.9 Hz, 1H), 5.08 (dt, *J* 10.3, 2.0 Hz, 1H), 4.90 (dd, *J* 17.1, 1.8 Hz, 1H), 4.85 (d, *J* 10.3 Hz, 1H), 4.36 (dd, *J* 14.7, 6.0 Hz, 1H), 4.03−3.95 (m, 1H), 3.06−2.89 (m, 2H), 2.40 (s, 3H), 1.34−1.19 (m, 4H), 0.82 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers) δ: 157.7, 157.5, 144.3, 143.6, 142.6, 141.9, 138.6, 137.8, 137.4, 136.8, 136.2, 134.5, 132.6, 132.3, 129.7, 129.6, 129.5, 129.2, 129.0, 128.9, 128.4, 128.4(×2), 127.9, 127.8, 127.7, 126.4, 119.8, 119.3, 117.8, 113.8, 54.9, 54.0, 53.1, 51.1, 40.0, 39.9, 32.4, 31.7, 29.4, 29.3, 21.6, 21.5, 20.0, 19.7, 13.8, 13.7; FTIR (film) *v*: 3345, 3083, 3027, 2957, 2929, 2871, 1631, 1561, 1348, 1163, 1092, 663, 580, 549 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{31}N_3O_3SNa$ [M + Na$^+$] 464.1984; Found 464.1992.

Methyl (1-Tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)carbamate (32a). Prepared in the same manner as compound **25a**; yield 36 mg (77%) starting from 50 mg of diene **31a**; white solid, mp 65−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* 8.1 Hz, 2H), 7.34−7.17 (m, 5H), 7.00 (d, *J* 6.8 Hz, 1H), 5.87 (s, 2H), 5.67 (d, *J* 10.6 Hz, 1H), 5.39−5.30 (m, 1H), 4.47 (s, 1H), 4.02 (s, 1H), 3.65 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 144.0, 140.9, 137.9, 137.6, 129.9, 128.8, 128.7, 128.4, 128.3, 128.03, 127.97, 127.3, 52.2, 48.9, 29.7, 21.6; FTIR (film) *v*: 3373, 3063, 3031, 2954, 2925, 2854, 1722, 1523, 1494, 1341, 1237, 1160, 715, 578 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{20}N_2O_4SNa$ [M + Na$^+$] 395.1041; Found 395.1045.

Methyl (9-Methyl-1-tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)carbamate (32b). Prepared in the same manner as compound **25a**; yield 37 mg (79%) starting from 50 mg of compound **31b**; white solid, mp 169−170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* 8.3 Hz, 2H), 7.37−7.28 (m, 3H), 7.23−7.18 (m, 1H), 7.18−7.15 (m, 1H), 6.47 (d, *J* 9.4 Hz, 1H), 5.98−5.90 (m, 1H), 5.71 (dd, *J* 11.5, 4.3 Hz, 1H), 5.34 (t, *J* 8.6 Hz, 1H), 4.47 (dd, *J* 19.1, 4.8 Hz, 1H), 3.64 (s, 3H), 2.45 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.3, 144.1, 141.7, 138.4, 136.9, 136.2, 131.3, 129.8, 129.7, 129.0, 128.8, 127.8, 126.8, 53.2, 52.1, 48.0, 21.6, 18.8; FTIR (film) v: 3376, 3024, 2953, 2935, 2853, 1717, 1508, 1333, 1319, 1236, 1153, 1091 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{22}N_2O_4SNa$ [M + Na$^+$] 409.1198; Found 409.1198.

Methyl (7-Methyl-1-tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)carbamate (32c). Prepared in the same manner as compound **25a**; yield 32 mg (69%) starting from 50 mg of diene **31c**; white solid, mp 180−181 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.82 (br d, *J* 7.4 Hz, 1H), 7.74 (d, *J* 8.0 Hz, 2H), 7.43 (d, *J* 8.0 Hz, 2H), 7.12 (d, *J* 8.0 Hz, 1H), 7.05 (d, *J* 8.0 Hz, 1H), 6.83 (s, 1H), 5.69−5.61 (m, 1H), 5.54 (br d, *J* 11.9 Hz, 1H), 5.40 (br dq, *J* 11.9, 2.9 Hz, 1H), 4.58 (br d, *J* 18.9 Hz, 1H), 3.69 (br d, *J* 18.9 Hz, 1H), 3.56 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 156.5, 144.0, 140.7, 138.4, 137.5, 137.2, 131.0, 130.5, 129.0, 128.9, 127.3, 126.1, 124.5, 52.0, 49.8, 49.0, 21.5, 20.8; FTIR (film) *v*: 3372, 2953, 2924, 2854, 1720, 1502, 1340, 1159, 1102, 690, 542 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{22}N_2O_4SNa$ [M + Na$^+$] 409.1198; Found 409.1209.

Methyl (8-Methyl-1-tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)carbamate (32d). Prepared in the same manner as compound **25a**; yield 39 mg (84%) starting from 50 mg of diene **31d**; white solid, mp 179−180 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.83 (d, *J* 8.9 Hz, 1H), 7.72 (d, *J* 8.0 Hz, 2H), 7.42 (d, *J* 8.0 Hz, 2H), 7.02 (d, *J* 7.9 Hz, 1H), 6.98 (s, 1H), 6.84 (d, *J* 7.9 Hz, 1H), 5.75−5.69 (m, 1H), 5.58−5.51 (m, 1H), 5.40 (dq, *J* 11.5, 2.9 Hz, 1H), 4.62 (br d, *J* 18.8 Hz, 1H), 3.67 (br d, *J* 18.8 Hz, 1H), 3.57 (s, 3H), 2.40 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 156.5, 144.0, 143.5, 138.4, 138.0, 134.8, 131.0, 130.5, 128.5, 128.0, 127.2, 126.2, 125.1, 52.0, 49.9, 49.1, 21.5, 21.4; FTIR (film) *v*: 3371, 2953, 2924, 2854, 1721, 1496, 1341, 1159, 1102, 677, 549 cm^{-1};HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{22}N_2O_4SNa$ [M + Na$^+$] 409.1198; Found 409.1205.

***t*-Butyl (1-Tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)carbamate (32e).** Yield 40 mg (77%) starting from 55 mg of diene **31e**; low melting waxy solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.74 (d, *J* 8.0 Hz, 2H), 7.59 (d, *J* 8.9 Hz, 1H), 7.43 (d, *J* 8.0 Hz, 2H), 7.31 (td, *J* 7.6, 1.3 Hz, 1H), 7.25−7.14 (m, 2H), 6.96 (d, *J* 7.7 Hz, 1H), 5.74−5.69 (m, 1H), 5.60−5.52 (m, 1H), 5.42−5.36 (m, 1H), 4.68−4.60 (m, 1H), 3.71−3.63 (m, 1H), 2.40 (s, 3H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 155.3, 144.3, 144.0, 138.5, 137.4, 131.0, 130.6, 128.5, 128.1, 128.0, 127.2, 125.9, 124.4, 78.6, 67.5, 49.2, 28.7, 21.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{26}N_2O_4SNa$ [M + Na$^+$] 437.1511; Found 437.1512.

***N*-(1-Tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)acetamide (32f).** Yield 31 (84%) starting from 40 mg of diene **31f**; off-white solid, mp 203−205 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.46 (d, *J* 8.8 Hz, 1H), 7.75 (d, *J* 8.3 Hz, 2H), 7.43 (d, *J* 8.3 Hz, 2H), 7.30 (td, *J* 7.5, 1.4 Hz, 1H), 7.25−7.17 (m, 2H), 6.99 (dd, *J* 7.7, 1.0 Hz, 1H), 6.03−5.97 (m, 1H), 5.57−5.51 (m, 1H), 5.48−5.42 (m, 1H), 4.67−4.59 (m, 1H), 3.75−3.67 (m, 1H), 2.40 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 169.0, 144.0, 143.6, 138.4, 137.7, 130.8, 130.5, 128.5, 128.2, 128.1, 127.3, 126.5, 124.7, 49.1, 47.8, 23.1, 21.5; FTIR (film) *v*: 3377, 3281, 3062, 3034, 2978, 2882, 2839, 1658, 1536, 1487, 1339, 1305, 1159, 1112, 1092, 897, 714, 656, 578, 533 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{20}N_2O_3SNa$ [M + Na$^+$] 379.1092; Found 379.1090.

1-Butyl-3-(1-tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)urea (32g). Yield 32 (68%) starting from 50 mg of diene **31g**; off-white solid, mp 163−164 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.76 (d, *J* 8.3 Hz, 2H), 7.43 (d, *J* 8.3 Hz, 2H), 7.30 (td, *J* 7.5, 1.3 Hz, 1H), 7.23−7.17 (m, 2H), 6.99−6.94 (m, 1H), 6.51 (d, *J* 9.3 Hz, 1H), 5.94 (t, *J* 5.7 Hz, 1H), 5.90−5.85 (m, 1H), 5.51 (dq, *J* 11.6, 2.4 Hz, 1H), 5.46−5.36 (m, 1H), 4.59 (dq, *J* 18.7, 3.0 Hz, 1H), 3.71 (dq, *J* 18.7, 2.7 Hz, 1H),

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3.02 (q, *J* 6.5 Hz, 2H), 2.40 (s, 3H), 1.42−1.24 (m, 4H), 0.87 (t, *J* 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 157.6, 144.8, 144.0, 138.5, 137.6, 132.1, 130.5, 128.4, 127.9, 127.3(×2), 126.1, 124.8, 49.2, 48.6, 32.6, 30.0, 21.5, 20.0, 14.2; FTIR (film) *v*: 3317, 3063, 3029, 2957, 2928, 2871, 1635, 1564, 1485, 1452, 1341, 1305, 1273, 1238, 1159, 1106, 897, 713, 653, 578, 544 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{22}H_{27}N_3O_3SNa$ [M + Na$^+$] 436.1671; Found 436.1670.

Methyl 2-(Allylthio)benzoate. Prepared in the same manner as compound **18a**; yield 4.14 g (67%) starting from 5 g of methyl thiosalicylate; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (dd, *J* 7.8, 1.6 Hz, 1H), 7.43−7.38 (m, 1H), 7.33−7.30 (m, 1H), 7.17−7.12 (m, 1H), 5.91 (ddt, *J* 17.0, 10.1, 6.6 Hz, 1H), 5.31 (dq, *J* 17.0, 1.4 Hz, 1H), 5.16 (dt, *J* 10.1, 1.2 Hz, 1H), 3.90 (s, 3H), 3.59 (dt, *J* 6.6, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.9, 141.1, 132.7, 132.1, 131.2, 128.0, 126.2, 124.0, 118.6, 52.0, 35.4; FTIR (film) *v*: 3081, 3005, 2979, 2959, 2842, 1714, 1464, 1434, 1277, 1251, 1062, 923, 743 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{11}H_{12}O_2SNa$ [M + Na$^+$] 231.0456; Found 231.0451.

(2-(Allylthio)phenyl)methanol. To a cooled to 0 °C solution of methyl 2-(allylthio)benzoate (4 g, 19.2 mmol) in 60 mL of dry THF was added a 2 M soln. of $LiAlH_4$ in THF (23.1 mmol, 11.5 mL). The progress of the reduction was followed by TLC. After 2 h, the reaction was quenched by addition of sat. Na_2SO_4. Solid was removed, and the solvent was removed under decreased pressure. The residue was chromatographed on silica gel (10% AcOEt in hexanes) to afford 2.9 g (84%) of a product as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41−7.37 (m, 2H), 7.28−7.20 (m, 2H), 5.87 (ddt, *J* 17.0, 10.0, 7.0 Hz, 1H), 5.13−5.04 (m, 2H), 4.78 (d, *J* 6.3 Hz, 2H), 3.54 (dd, *J* 7.0, 0.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.3, 134.0, 133.3, 131.1, 128.3, 128.2, 127.0, 117.9, 63.7, 37.7; FTIR (film) *v*: 3370, 3081, 3060, 2917, 2878, 1635, 1590, 1467, 1442, 1426, 1194, 1066, 1035, 989, 921, 750 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{12}OS$ 180.0609; Found 180.0610.

2-(Allylthio)benzaldehyde. Prepared in the same manner as compound **18f**; yield 1.66 g (64%) starting from 2.6 g of (2-(allylthio)phenyl)methanol; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.39 (s, 1H), 7.83 (dd, *J* 7.7, 1.6 Hz, 1H), 7.52−7.47 (m, 1H), 7.43 (dd, *J* 7.9, 1.1 Hz, 1H), 7.34−7.28 (m, 1H), 5.87 (ddt, *J* 16.9, 10.0, 6.8 Hz, 1H), 5.16 (dq, *J* 16.9, 1.4 Hz, 1H), 5.11 (dq, *J* 10.0, 1.0 Hz, 2H), 3.57 (dt, *J* 6.8, 1.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.6, 140.8, 134.7, 133.8, 132.5, 131.5, 129.7, 126.0, 118.7, 36.9; FTIR (film) *v*: 3081, 3060, 2955, 2923, 2852, 2738, 1692, 1587, 1460, 1197, 924, 752 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{10}OS$ [M] 178.0452; Found 178.0453.

Ethyl (*E*)-3-(2-(Allylthio)phenyl)acrylate. Prepared in the same manner as compound **19a**; yield 1.54 g (69%) starting from 1.6 g of 2-(allylthio)benzaldehyde; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, *J* 16.0 Hz, 1H), 7.53 (d, *J* 7.7 Hz, 1H), 7.39 (d, *J* 7.8 Hz, 1H), 7.29−7.23 (m, 1H), 7.22−7.16 (m, 1H), 6.34 (d, *J* 15.9 Hz, 1H), 5.87−5.74 (m, 1H), 5.06−4.97 (m, 2H), 4.24 (q, *J* 7.1 Hz, 2H), 3.50−3.41 (m, 2H), 1.31 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 142.1, 136.6, 135.9, 133.1, 131.9, 130.0, 127.1, 127.1, 120.1, 117.9, 60.4, 38.0, 14.3; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{16}O_2SNa$ [M + Na$^+$] 271.0769; Found 271.0767.

(*E*)-3-(2-(Allylthio)phenyl)prop-2-en-1-ol (34). Prepared in the same manner as compound **20a**; yield 1.01 g (81%) starting from 1.5 g of ethyl (*E*)-3-(2-(allylthio)phenyl)acrylate; yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50−7.44 (m, 1H), 7.39−7.33 (m, 1H), 7.22−7.11 (m, 3H), 6.28 (dt, *J* 15.8, 5.7 Hz, 1H), 5.84 (ddt, *J* 16.9, 10.0, 6.9 Hz, 1H), 5.11−5.01 (m, 2H), 4.34 (dd, *J* 5.7, 1.3 Hz, 2H), 3.48 (d, *J* 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.0, 134.1, 133.3, 131.3, 130.7, 128.8, 127.8, 126.9, 126.4, 117.7, 63.8, 37.5; FTIR (film) v: 3340, 3080, 3056, 3010, 2916, 2862, 1636, 1585, 1462, 1435, 1228, 1090, 1010, 987, 968, 921, 748 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{14}OSNa$ [M + Na$^+$] 229.0663; Found 229.0662.

(*E*)-3-(2-(Allylthio)phenyl)allyl Carbamate (35). Prepared in the same manner as compound **21a**; yield 975 mg (81%) starting from 1 g of allyl alcohol **34**; white solid, mp 40−41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48−7.44 (m, 1H), 7.38−7.33 (m, 1H), 7.22−7.16 (m, 3H), 6.20 (dt, *J* 15.8, 6.2 Hz, 1H), 5.83 (ddt, *J* 16.9, 10.0, 7.0 Hz, 1H), 5.11−4.98 (m, 4H), 4.75 (dd, *J* 6.2, 1.4 Hz, 2H), 3.50−3.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.0, 137.7, 134.3, 133.3, 131.6, 131.4, 128.1, 127.0, 126.5, 125.7, 117.8, 65.6, 37.6; FTIR (film) *v*: 3485, 3348, 3080, 3056, 3011, 2978, 2946, 1714, 1600, 1402, 1335, 1052, 750 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{15}NO_2SNa$ [M + Na$^+$] 272.0721; Found 272.0723.

Methyl (1-(2-(Allylthio)phenyl)allyl)carbamate (36). Prepared as compound **24a**; yield 138 mg (73%) starting from 180 mg of allyl carbamate **35**; white solid, mp 71−72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43−7.39 (m, 1H), 7.26−7.19 (m, 3H), 5.99 (ddd, *J* 16.9, 10.4, 4.7 Hz, 1H), 5.91−5.79 (m, 2H), 5.42 (s, 1H), 5.21−5.00 (m, 4H), 3.64 (s, 3H), 3.54−3.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 141.6, 137.7, 134.6, 133.4, 132.2, 128.0, 127.6, 127.2, 117.8, 115.7, 55.1, 52.2, 38.3; FTIR (film) *v*: 3328, 3083, 3060, 3010, 2963, 2923, 1705, 1510, 1232, 1198, 922, 757 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_2SNa$ [M + Na$^+$] 286.0878; Found 286.0878.

Methyl (1-(2-(Allylsulfonyl)phenyl)allyl)carbamate (38). To a solution of carbamate **36** (230 mg, 0.87 mmol) in 20 mL of CH_2Cl_2 cooled to −5 °C was added a solution of *m*-CPBA (430 mg, 1.92 mmol) in 10 mL of CH_2Cl_2. After 5 h, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. aq. $NaHCO_3$. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was chromatographed on silica gel (10% to 30% AcOEt in hexanes) to provide 210 mg (81%) of product **38** as white solid. mp 112−113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (dd, *J* 8.0, 1.4 Hz, 1H), 7.65−7.58 (m, 1H), 7.47 (dd, *J* 7.9, 1.2 Hz, 1H), 7.45−7.39 (m, 1H), 6.21−6.14 (m, 1H), 6.05 (ddd, *J* 17.3, 10.4, 4.7 Hz, 1H), 5.86−5.74 (m, 1H), 5.55−5.44 (m, 1H), 5.33−5.18 (m, 3H), 5.08 (dd, *J* 17.3, 1.8 Hz, 1H), 4.45−4.34 (m, 1H), 4.12 (dd, *J* 14.5, 6.5 Hz, 1H), 3.64 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 142.3, 137.4, 136.1, 134.0, 131.4, 128.7, 127.6, 124.9, 124.6, 116.2, 60.5, 53.0, 52.4; FTIR (film) *v*: 3360, 3088, 3024, 2969, 2916, 1715, 1522, 1314, 1285, 1252, 1145, 1117, 935, 765, 6329, 537 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_4SNa$ [M + Na$^+$] 318.0776; Found 318.0773.

Methyl (1,1-Dioxido-2,5-dihydrobenzo[*b*]thiepin-5-yl)carbamate (39). Prepared in the same manner as compound **25a**; yield 44 mg (90%) starting from 50 mg of diene **38**; off-white solid, mp 185−186 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.26 (d, *J* 8.8 Hz, 1H), 7.90 (dd, *J* 7.8, 1.4 Hz, 1H), 7.74 (td, *J* 7.6, 1.4 Hz, 1H), 7.57−7.52 (m, 1H), 7.45 (d, *J* 7.8 Hz, 1H), 6.48−6.42 (m, 1H), 5.82 (dq, *J* 12.3, 2.2 Hz, 1H), 5.57−5.49 (m, 1H), 4.31−4.22 (m, 1H), 4.04−3.96 (m, 1H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 138.1, 137.6, 134.6, 131.3, 130.4, 128.7, 128.3, 119.6, 54.9, 54.6, 52.3; FTIR (film) *v*: 3336, 3065, 2993, 2951, 294, 2847, 1712, 1534, 1301, 1273, 1174, 1141, 1119, 1045, 737, 697, 533 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{13}NO_4SNa$ [M + Na$^+$] 290.0463; Found 290.0461.

(*E*)-4-(2-(Allyloxy)phenyl)but-3-en-2-one (41). A solution of aldehyde **18a** (2.3 g, 14.2 mmol) and 1-triphenylphosphoranylidene-2-propanone (18.4 mmol, 5.87 g) in dry toluene (50 mL) was stirred overnight at 40 °C. After removal of the solvent, the residue was purified by column chromatography on silica gel (15% AcOEt in hexanes) to afford enone **41** (2.15 g, 75%) as a yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* 16.5 Hz, 1H), 7.55 (dd, *J* 7.7, 1.7 Hz, 1H), 7.36−7.30 (m, 1H), 6.97 (t, *J* 7.6 Hz, 1H), 6.91 (d, *J* 8.3 Hz, 1H), 6.75 (d, *J* 16.5 Hz, 1H), 6.08 (ddt, *J* 17.3, 10.6, 5.2 Hz, 1H), 5.43 (dq, *J* 17.3, 1.6 Hz, 1H), 5.32 (dq, *J* 10.6, 1.4 Hz, 1H), 4.63 (dt, *J* 5.1, 1.5 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.9, 157.3, 138.6, 132.8, 131.6, 128.3, 127.8, 123.7, 121.0, 117.8, 112.6, 69.2, 27.1; FTIR (film) *v*: 3074, m3023, 2920, 2869, 1688, 1667, 1599, 1486, 1454, 1359, 1299, 1243, 993, 753 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{13}H_{14}O_2Na$ [M + Na$^+$] 225.0891; Found 225.0891.

(*E*)-4-(2-(Allyloxy)phenyl)but-3-en-2-ol (*rac*-42). $NaBH_4$ (202 mg, 5.34 mmol) was added to a mixture of enone **41** (900 mg, 4.45 mmol) and $CeCl_3{\cdot}7H_2O$ (1.99 g, 5.34 mmol) in CH_2Cl_2 (8 mL) and MeOH (3.2 mL). When the reaction was completed, the solvents were removed and the residue was partitioned between CH_2Cl_2 and water. The aqueous layer was washed with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After

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removal of the solvent, the residue was purified by flash chromatography on silica gel (10% to 20% AcOEt in hexanes) to provide 735 mg (81%) of allyl alcohol ***rac*-42** as a colorless oil; ^{1}H NMR (500 MHz, C_6D_6) δ 7.40 (dd, *J* 7.6, 1.4 Hz, 1H), 7.11 (d, *J* 16.1 Hz, 1H), 7.06−7.00 (m, 1H), 6.83 (t, *J* 7.5 Hz, 1H), 6.57 (d, *J* 8.2 Hz, 1H), 6.26 (dd, *J* 16.1, 6.4 Hz, 1H), 5.79 (ddt, *J* 17.2, 10.4, 5.1 Hz, 1H), 5.21 (dq, *J* 17.2, 1.6 Hz, 1H), 5.05−5.00 (m, 1H), 4.32−4.25 (m, 1H), 4.14 (d, *J* 5.1 Hz, 2H), 1.24 (d, *J* 6.4 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ: 156.2, 135.2, 133.8, 128.5, 127.2, 126.8, 124.0, 121.1, 117.0, 112.6, 69.1, 69.0, 23.6; FTIR (film) *v*: 3368, 3074, 3032, 2972, 2869, 1598, 1488, 1451, 1240, 1052, 1021, 976, 937, 751 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{16}O_2$ [M] 204.1150; Found 204.1154; HPLC: Chiralpak OD-H, 10% *i*-PrOH in hexanes, 1 mL/min, 254 nm; R_t 15.97 (*R* enantiomer) and 27.44 min (*S* enantiomer).

Kinetic Resolution of *rac*-42. A suspension of alcohols ***rac*-42** (730 mg, 1.75 mmol), *Candida antartica* lipase (55 mg), 4 Å molecular sieves (300 mg), and vinyl acetate (8.2 mL) in pentane (16 mL) was stirred overnight. The progress of the reaction was followed by ^{1}H NMR. The reaction mixture was then filtered through Celite, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (10% to 30% AcOEt/hexanes) to afford 439 mg of acetate **43** (45%, 86.2% *ee* determined after hydrolysis) and 252 mg of alcohol **(*S*)-42** (39%, 99% *ee*). **(*S*,*E*)-4-(2-(allyloxy)phenyl)but-3-en-2-ol ((*S*)-42)**: HPLC: Chiralpak OD-H: 10% *i*-PrOH in hexanes, 1 mL/min R_t 15. 24 min (5.5%, *R*) and 26.31 min (94.5%, *S*); 99% *ee*; $[\alpha]_D^{21}$ −17.4 (*c* 1.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (dd, *J* 7.6, 1.6 Hz, 1H), 7.23−7.16 (m, 1H), 6.96−6.89 (m, 2H), 6.86 (d, *J* 8.3 Hz, 1H), 6.28 (dd, *J* 16.1, 6.7 Hz, 1H), 6.08 (ddt, *J* 17.3, 10.5, 5.2 Hz, 1H), 5.42 (dq, *J* 17.3, 1.6 Hz, 1H), 5.29 (dq, *J* 10.5, 1.4 Hz, 1H), 4.57 (dt, *J* 5.1, 1.5 Hz, 2H), 4.54−4.45 (m, 1H), 1.37 (d, *J* 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.8, 134.2, 133.4, 128.6, 126.9, 126.0, 124.3, 120.9, 117.3, 112.4, 69.4, 69.2, 23.4; FTIR (film) *v*: 3373, 3074, 3032, 2971, 2925, 2869, 1598, 1488, 1451, 1292, 1240, 1224, 1092, 1021, 997, 976, 937, 751 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{13}H_{16}O_2$ [M] 204.1150; Found 204.1143. **(*R*,*E*)-4-(2-(allyloxy)phenyl)but-3-en-2-yl acetate (43)**: $[\alpha]_D^{22}$ +53.7 (*c* 1.51, $CHCl_3$) (86.2% *ee* determined for free alcohol); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (dd, *J* 7.7, 1.7 Hz, 1H), 7.22−7.17 (m, 1H), 6.96 (d, *J* 16.1 Hz, 1H), 6.94−6.89 (m, 1H), 6.85 (dd, *J* 8.3, 1.1 Hz, 1H), 6.23 (dd, *J* 16.1, 6.8 Hz, 1H), 6.07 (ddt, *J* 17.3, 10.4, 5.1 Hz, 1H), 5.54 (pd, *J* 6.5, 1.2 Hz, 1H), 5.43 (dq, *J* 17.3, 1.7 Hz, 1H), 5.29 (dq, *J* 10.6, 1.5 Hz, 1H), 4.56 (dt, *J* 5.1, 1.6 Hz, 2H), 2.07 (s, 3H), 1.41 (d, *J* 6.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.3, 155.9, 133.3, 129.3, 128.8, 126.9, 126.3, 125.7, 120.9, 117.2, 112.4, 71.5, 69.1, 21.4, 20.4; FTIR (film) *v*: 3074, 3032, 2979, 2930, 2870, 1736, 1598, 1489, 1451, 1370, 1241, 1041, 1019, 751 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{15}H_{18}O_3$ [M] 246.1256; Found 246.1256.

(*R*,*E*)-4-(2-(Allyloxy)phenyl)but-3-en-2-ol ((*R*)-42). To a solution of acetate **43** (430 mg, 1.75 mmol) in MeOH (13 mL) and H_2O (3 mL) was added K_2CO_3 (965 mg, 7 mmol), and the resulting mixture was kept at ambient temperature. The progress of hydrolysis was followed by TLC (20% AcOEt/hexanes). After stirring overnight, MeOH was removed under reduced pressure and the aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel (20% AcOEt/hexanes) to afford 258 mg of alcohol **(*R*)-42** (67%). *ee* 86.2% according to HPLC. HRMS (EI) *m*/*z* calcd for $C_{13}H_{16}O_2$ [M] 204.1150; Found 204.1144.

(S)-2-(3-((*tert*-Butyldiphenylsilyl)oxy)but-1-yn-1-yl)phenyl Acetate (49). *O*-TBDPS-(*S*)-3-butyn-2-ol (353 mg, 1.14 mmol) was added to a mixture of 2-acetoxy-iodobenzene (300 mg, 1.14 mmol), $Pd(Ph_3P)_2Cl_2$ (40 mg, 0.06 mmol), and CuI (22 mg, 0.11 mmol) in 10 mL of Et_3N. The resulting mixture was stirred overnight at rt. Next, solvent was removed and the residue was chromatographed on silica gel (1% AcOEt in hexanes) to afford 427 mg (84%) of products **49** as a yellowish oil; $[\alpha]_D^{23}$ −165.9 (*c* 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80−7.77 (m, 2H), 7.74−7.70 (m, 2H), 7.45−7.29 (m, 8H), 7.18−7.13 (m, 1H), 7.08−7.04 (m, 1H), 4.69 (q, J 6.5 Hz, 1H), 2.24 (s, 3H), 1.48 (d, J 6.5 Hz, 3H), 1.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.8, 151.5, 139.4, 135.9, 135.8, 133.7, 129.8, 129.7, 129.4, 129.2, 127.7, 127.6, 125.7, 122.2, 117.2, 96.6, 78.6, 60.4, 60.4, 26.9, 25.3, 20.8; FTIR (film) *v*: 3071, 2959, 2931, 2858, 1768, 1487, 1428, 1368, 1207, 1186, 1103, 703, 506 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{28}H_{30}O_3SiNa$ [M + Na$^+$] 465.1862; Found 465.1859.

(*S*)-4-(2-(Allyloxy)phenyl)but-3-yn-2-ol (50). A 7 M soln. of NH_3 in MeOH (390 μL, 2.71 mmol) was added to a solution of **49** (300 mg, 0.68 mmol) in 10 mL of dry MeOH. After stirring overnight, solvent and volatiles were removed under deacresed pressure. The residue was dissolved in 10 mL of DMF, and K_2CO_3 (215 mg, 1.56 mmol) and allyl bromide (164 mg, 117 μL, 1.36 mmol) were added. After 15 h, the reaction mixture was dilluted with water and the resulting mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, and solvent was removed. The residue was disolved in 20 mL of dry THF, and a 1 M soln. of TBAF in THF (0.75 mmol, 750 μL) was added. After 3 h, solvent was removed and the residue was chromatographed on silica gel (10% to 20% AcOEt in hexanes) to afford 85 mg (62%) of product **50** as colorless oil. $[\alpha]_D^{21}$ −21.5 (*c* 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42−7.35 (m, 1H), 7.27−7.20 (m, 1H), 6.93−6.80 (m, 2H), 6.13−6.00 (m, 1H), 5.48 (d, *J* 17.3 Hz, 1H), 5.28 (d, *J* 10.7 Hz, 1H), 4.83−4.75 (m, 1H), 4.63−4.54 (m, 2H), 1.55 (d, *J* 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.1, 134.8, 133.6, 133.0, 129.6, 120.7, 117.2, 112.5, 95.3, 80.3, 69.3, 58.9, 24.4; HRMS (EI) *m*/*z* calcd for $C_{13}H_{14}O_2$ [M] 202.0994; Found 202.0984.

(*S*,*E*)-4-(2-(Allyloxy)phenyl)but-3-en-2-ol ((S)-42) − Method 2. A 2 M soln. of $LiAlH_4$ (0.25 mmol, 125 μL) was added to a solution of **50** (50 mg, 0.25 mmol) in dry THF. After 2 h, reaction was quenched by addition of sat. Na_2SO_4 and diluted with Et_2O. Precipitation was filtered, and solvent was removed. The residue was chromatographed on silica gel (10% to 20% AcOEt in hexanes) to afford 43 mg (85%) of **(*S*)-42** (*ee* 96.7%, R_t 25.7 min, Chiralpak OD-H, 10% IPA/hexanes, 1 mL/min, 254 nm).

(*S*,*E*)-4-(2-(Allyloxy)phenyl)but-3-en-2-yl Carbamate (51). Prepared in the same manner as compound **21i**; yield 148 mg (61%) starting from 200 mg of allyl alcohol **(*S*)-42**; white solid, mp 96−97 °C; $[\alpha]_D^{23}$ −27.6 (*c* 0.53, $CHCl_3$), 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (dd, *J* 7.7, 1.7 Hz, 1H), 7.22−7.16 (m, 1H), 6.97 (d, *J* 16.1 Hz, 1H), 6.91 (t, *J* 7.5 Hz, 1H), 6.85 (d, *J* 16.1 Hz, 1H), 6.24 (dd, *J* 16.2, 6.5 Hz, 1H), 6.07 (ddt, *J* 17.2, 10.4, 5.1 Hz, 1H), 5.28 (dq, *J* 10.4, 1.5 Hz, 1H), 4.89 (s, 2H), 4.56 (dt, *J* 5.2, 1.7 Hz, 2H), 1.42 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.6, 155.9, 133.3, 129.6, 128.8, 127.0, 126.1, 125.8, 120.9, 117.3, 112.5, 72.2, 69.2, 20.6; FTIR (film) *v*: 3425, 3334, 3269, 3214, 3076, 3018, 2973, 2927, 2867, 1687, 1615, 1489, 1450, 1400, 1359, 1302, 1244, 1151, 1100, 1042, 1021, 973, 751, 591 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{17}NO_3Na$ [M + Na$^+$] 270.1106; Found 270.1104.

Methyl (*S*,*E*)-(1-(2-(Allyloxy)phenyl)but-2-en-1-yl)carbamate (53). Prepared in the same manner as compound **24a**; yield 42 mg (65%) starting from 60 mg of allyl carbamate **51**; colorless oil; $[\alpha]_D^{21}$ −9.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27−7.18 (m, 2H), 6.92 (t, *J* 7.4 Hz, 1H), 6.87 (d, *J* 8.1 Hz, 1H), 6.05 (ddt, *J* 17.4, 10.3, 5.1 Hz, 1H), 5.73−5.53 (m, 3H), 5.45−5.37 (m, 2H), 5.29 (dd, *J* 10.5, 1.6 Hz, 1H), 4.60−4.56 (m, 2H), 3.65 (s, 3H), 1.66 (d, *J* 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.2, 155.9, 133.0, 130.8, 129.8, 128.58, 128.55, 126.2, 121.1, 117.5, 112.4, 68.9, 54.9, 52.0, 17.6; HRMS (ESI-TOF) *m*/*z* calcd for $C_{15}H_{19}NO_3Na$ [M + Na$^+$] 284.1283; Found 284.1262.

Methyl (S)-(2,5-Dihydrobenzo[*b*]oxepin-5-yl)carbamate (55). Prepared in the same manner as compound **32a**; yield 22 mg (77% starting from 34 mg of diene **53**; off-white solid; mp 135−136 °C; $[\alpha]_D^{22}$ +103.1 (*c* 0.33, $CHCl_3$); HRMS (ESI-TOF) *m*/*z* calcd for $C_{12}H_{13}NO_3Na$ [M + Na$^+$] 242.0793; Found 242.0791.

(*E*)-*N*-Allyl-4-methyl-*N*-(2-(3-oxobut-1-en-1-yl)phenyl)-benzenesulfonamide (44). Prepared in the same manner as compound **41**; yield 2.6 g (76%) starting from 3.0 g of aldehyde **27a**; white solid, mp 106−107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* 16.6 Hz, 1H), 7.68 (dd, *J* 7.8, 1.6 Hz, 1H), 7.57 (d, *J* 8.3 Hz, 2H), 7.34 (td, *J* 7.6, 1.4 Hz, 1H), 7.31−7.25 (m, 3H), 6.80 (dd, *J* 7.9, 1.4 Hz, 1H), 6.57 (d, *J* 16.6 Hz, 1H), 5.72 (ddt, *J* 16.9, 10.1, 6.7 Hz,

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1H), 5.05−4.96 (m, 2H), 4.43−4.26 (m, 1H), 4.03−3.88 (m, 1H), 2.43 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 198.8, 143.9, 139.6, 138.6, 135.8, 135.6, 132.0, 130.5, 129.64, 129.56, 129.2, 128.8, 127.9, 127.1, 119.9, 54.9, 26.5, 21.5; FTIR (film) ν: 3066, 3030, 2922, 2867, 1672, 1609, 1483, 1454, 1351, 1254, 1165, 1092, 1061, 980, 869, 816, 725, 665, 576, 548 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{21}NO_3SNa$ [M + Na$^+$] 378.1140; Found 378.1141.

(*E*)-*N*-Allyl-*N*-(2-(3-hydroxybut-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (*rac*-45). The reaction was performed in the same manner as the reduction of enone **41**; yield 930 mg (71%) starting from 1.3 g of enone **44**; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61−7.56 (m, 3H), 7.30−7.24 (m, 3H), 7.12 (td, J 7.7, 1.6 Hz, 1H), 6.78−6.71 (m, 2H), 6.21 (dd, J 16.0, 6.5 Hz, 1H), 5.73 (ddt, J 16.9, 10.2, 6.7 Hz, 1H), 5.02−4.94 (m, 2H), 4.47−4.38 (m, 1H), 4.27−4.15 (m, 1H), 4.06−3.94 (m, 1H), 2.44 (s, 3H), 1.33 (d, J 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.5, 137.7, 136.7, 136.4, 135.7, 132.5, 129.6, 129.5, 128.5, 127.9, 127.8, 126.4, 125.2, 119.2, 69.0, 54.8, 23.1, 21.5; FTIR (film) ν: 3498, 3409, 3065, 3028, 2972, 2935, 2869, 1597, 1484, 1450, 1346, 1164, 1092, 1061, 868, 816, 725, 664, 577, 548 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{23}NO_3SNa$ [M + Na$^+$] 380.1296; Found 380.1300; HPLC: column Chiralpak OD-H, 10% *i*-PrOH in hexanes, 1 mL/min, 254 nm, R_t 12.86 (*R*) and 15.76 min (*S*).

Kinetic Resolution of *rac*-45. Performed in the same manner as the kinetic resolution of alcohol *rac*-**42**; yield 474 mg (47%) of acetate **46** and 440 mg (49%) of allyl alcohol (*S*)-**45** starting from 90 mg of *rac*-**45**; **(*R*,*E*)-4-(2-((*N*-allyl-4-methylphenyl)sulfonamido)phenyl)-but-3-en-2-yl acetate (46)**: colorless oil; *ee* 93.3% (for free alcohol (*R*)-**45**); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (d, J 8.1 Hz, 2H), 7.56 (dd, J 7.9, 1.5 Hz, 1H), 7.29−7.23 (m, 3H), 7.14 (td, J 7.7, 1.6 Hz, 1H), 6.80−6.75 (m, 2H), 6.19−6.10 (m, 1H), 5.79−5.66 (m, 1H), 5.50−5.39 (m, 1H), 5.01−4.94 (m, 2H), 4.25−3.99 (m, 2H), 2.43 (s, 3H), 2.08 (s, 3H), 1.36 (d, J 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.2, 143.5, 137.3, 136.9, 136.4, 132.5, 132.4, 130.8, 129.7, 129.5, 128.5, 128.0, 127.8, 126.3, 119.2, 55.3, 54.7, 21.5, 21.3, 20.1; FTIR (film) ν: 3066, 3028, 2980, 2930, 2871, 1736, 1484, 1451, 1350, 1240, 1165, 1092, 1042, 817, 725, 664, 578 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{25}NO_4SNa$ [M + Na$^+$] 422.1402; Found 422.1398; **(*S*,*E*)-*N*-allyl-*N*-(2-(3-hydroxybut-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide ((*S*)-45)**: colorless oil; $[\alpha]_D^{22}$ −11.3 (c 0.26, $CHCl_3$); *ee* > 99% (HPLC, R_t 16.1 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60−7.56 (m, 3H), 7.29−7.23 (m, 3H), 7.12 (td, J 7.7, 1.6 Hz, 1H), 6.78−6.70 (m, 2H), 6.21 (dd, J 16.0, 6.5 Hz, 1H), 5.73 (ddt, J 16.9, 10.2, 6.7 Hz, 1H), 5.01−4.94 (m, 2H), 4.46−4.38 (m, 1H), 4.26−3.95 (m, 2H), 2.43 (s, 3H), 1.74 (s, 1H), 1.33 (d, J 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.5, 137.7, 136.7, 136.3, 135.7, 132.4, 129.6, 129.5, 128.5, 127.9, 127.8, 126.4, 125.1, 119.3, 68.9, 54.8, 23.1, 21.5; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{23}NO_3SNa$ [M + Na$^+$] 380.1296; Found 380.1296.

(*S*,*E*)-4-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)phenyl)-but-3-en-2-yl Carbamate (52). Prepared in the same manner as compound **21i**; yield 283 mg (60%) starting from 420 mg of allyl alcohol (*S*)-**45**; colorless oil; $[\alpha]_D^{22}$ −22.5 (c 1.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61−7.58 (m, 2H), 7.55 (dd, J 7.9, 1.4 Hz, 2H), 7.30−7.23 (m, 3H), 7.14 (td, J 7.2, 1.5 Hz, 1H), 6.78 (d, J 16.3 Hz, 1H), 6.78 (dd, J 7.9, 1.0 Hz, 1H), 6.22−6.11 (m, 1H), 5.73 (ddt, J 16.9, 10.2, 6.7 Hz, 1H), 5.40−5.31 (m, 1H), 5.04−4.94 (m, 2H), 4.66 (s, 2H), 4.23−3.98 (m, 2H), 2.43 (s, 3H), 1.37 (d, J 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.1, 143.5, 140.5, 137.4, 136.9, 136.5, 134.4, 132.5, 129.7, 129.5, 128.5, 128.0, 127.8, 126.4, 119.2, 54.7, 21.5; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{24}N_2O_4SNa$ [M + Na$^+$] 423.1354; Found 423.1351.

Methyl (*S*,*E*)-(1-(2-((*N*-Allyl-4-methylphenyl)sulfonamido)-phenyl)but-2-en-1-yl)carbamate (54). Prepared in the same manner as compound **24a**; yield 135 mg (87%) starting from 150 mg of carbamate **52**; colorless oil; $[\alpha]_D^{23}$ −46.5 (c 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6, mixture of rotamers, data for major rotamer) δ: 7.59−7.55 (m, 3H), 7.44−7.39 (m, 3H), 7.30 (td, J 7.5, 1.3 Hz, 1H), 7.14 (td, J 7.6, 1.7 Hz, 1H), 6.58 (dd, J 8.0, 1.3 Hz, 1H), 5.71−5.33 (m, 4H), 4.99−4.85 (m, 2H), 4.30 (dd, J 14.6, 5.7 Hz, 1H), 4.00 (dd, J 14.6, 7.5 Hz, 1H), 3.50 (s, 3H), 2.40 (s, 4H), 1.63 (d, J 5.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$, mixture of rotamers, data for major rotamer) δ: 156.4, 143.6, 142.7, 137.0, 132.3, 130.6, 129.5, 129.0, 128.7, 128.3, 128.2, 127.8, 126.9, 125.5, 119.4, 69.5, 55.0, 53.8, 29.3, 17.6; FTIR (film) ν: 3377, 3064, 3029, 2956, 2919, 2883, 1720, 2883, 1720, 1521, 1348, 1252, 1248, 1163, 1092, 1068, 663, 575 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{26}N_2O_4S$ [M + Na$^+$] 437.1511; Found 437.1505.

Methyl (*S*)-(1-Tosyl-2,5-dihydro-1*H*-benzo[*b*]azepin-5-yl)-carbamate (56). Prepared in the same manner as compound **25a**; yield 33 mg (74%) starting from 50 mg of diene **54**; $[\alpha]_D^{21.5}$ +87.0 (c 0.36, $CHCl_3$, *ee* > 99%); HRMS (ESI-TOF) m/z calcd for $C_{19}H_{20}N_2O_4SNa$ [M + Na$^+$] 395.1041; Found 395.1045.

Methyl 4-(4′-Fluorophenyl)-2-hydroxybenzoate (57).[33b,56] 4-Fluorophenylboronic acid (1.48 g, 10.57 mmol), Cs_2CO_3 (5.84 g, 17.62 mmol), and Pd(dppf)Cl_2 (260 mg, 0.35 mmol) were added to a degassed solution of methyl 2-hydroxy-4-iodobenzoate (2.0 g, 7.05 mmol) in 1,4-dioxane (67 mL) and water (4 mL). The solution was heated to 80 °C for 18 h, cooled to room temperature, and concentrated *in vacuo*. The reaction mixture was purified by flash column chromatography (elution with 5% AcOEt/hexanes) to yield methyl 4-(4′-fluorophenyl)-2-hydroxybenzoate (1.36 g, 78%) as a white solid. mp 115−117 °C (Lit.[33b,56] 110−112 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.80 (s, 1H), 7.88 (d, J 8.3 Hz, 1H), 7.61−7.53 (m, 2H), 7.17−7.10 (m, 3H), 7.07 (dd, J 8.3, 1.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.4, 164.3, and 161.84 (d, $J_{C\text{-}F}$ 248.3 Hz), 161.8, 147.4, 135.76, and 135.73 (d, $J_{C\text{-}F}$ 3.2 Hz), 130.4, 128.90, and 128.8 (d, $J_{C\text{-}F}$ 8.2 Hz), 115.9 ad 115.7 (d, $J_{C\text{-}F}$ 21.6 Hz), 115.60, 115.59, 111.2, 52.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.7; FTIR (film) ν: 3149, 3065, 3021, 2965, 1679, 1494, 1442, 1350, 1217, 1169, 1097, 840, 778, 717, 703 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{10}O_3F$ [M − H$^-$] 245.0614; Found 245.0617.

Methyl 3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-carboxylate.[33b] To a stirred solution of methyl salicylate **57** (1.71 g, 6.96 mmol) in anhydrous DMF (18 mL) were added anhydrous K_2CO_3 (1.44 g, 10.44 mol) and allyl bromide (1.26 g, 0.9 mL, 10.44 mmol). The resulting mixture was stirred until complete consumption of the starting material was achieved, as determined by TLC. The postreaction mixture was then diluted with AcOEt and washed with water (3×) and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness *in vacuo*. The product was isolated by flash column chromatography using 1% AcOEt/hexanes mixture as the eluent. White solid, mp 59−60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J 8.0 Hz, 1H), 7.57−7.51 (m, 2H), 7.17−7.09 (m, 4H), 6.10 (ddt, J 17.2, 10.6, 4.9 Hz, 1H), 5.54 (dq, J 17.2, 1.7 Hz, 1H), 5.33 (dq, J 10.6, 1.5 Hz, 1H), 4.70 (dt, J 4.8, 1.6 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 164.3, and 161.9 (d, $J_{C\text{-}F}$ 247.8 Hz), 158.7, 145.6, 136.43, and 136.40 (d, $J_{C\text{-}F}$ 3.2 Hz), 132.9, 132.5, 129.06, and 128.98 (d, $J_{C\text{-}F}$ 8.2 Hz), 119.4, 119.3, 117.7, 116.1, and 115.9 (d, $J_{C\text{-}F}$ 21.6 Hz), 112.6, 69.86, 52.1; FTIR (film) ν: 3076, 319, 2992, 2950, 1727, 1607, 1520, 1494, 1436, 1393, 1296, 1250, 1223, 1163, 1090, 998, 931, 827, 780, 771, 521 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}FO_3Na$ [M + Na$^+$] 309.0903; Found 309.0902.

(3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)methanol.[33b] Prepared in the same manner as (2-(allylthio)phenyl)methanol; yield 2 g (85%) starting from 2.6 g of methyl 3-(allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-carboxylate; white solid, mp 65−67 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.55−7.48 (m, 2H), 7.36 (d, J 7.7 Hz, 1H), 7.16−7.09 (m, 3H), 7.03 (d, J 1.5 Hz, 1H), 6.10 (ddt, J 17.2, 10.6, 5.2 Hz, 1H), 5.45 (dq, J 17.3, 1.6 Hz, 1H), 5.33 (dq, J 10.6, 1.4 Hz, 1H), 4.76 (s, 2H), 4.67 (dt, J 5.2, 1.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.5 and 162.3 (d, J 246.8 Hz), 156.7, 141.2, 137.14, and 137.12 (d, J 3.1 Hz), 132.9, 129.1, 128.69, and 128.63 (d, J 8.1 Hz), 128.4, 119.6, 117.8, 115.7, and 115.5 (d, J 21.5 Hz), 110.4, 68.9, 61.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ: −115.4 ppm; FTIR (film) ν: 3348, 3092, 2919, 2891, 2851, 1609, 1599, 1573, 1497, 1425, 1391, 1305, 1224, 1002, 820 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{15}O_2FNa$ [M + Na$^+$] 281.0954; Found 281.0952.

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3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-carbaldehyde.[33b] Prepared in the same manner as compound **18g**; yield 1.85 g (93%) starting from 2 g of (3-(allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)methanol; white solid, mp 50−51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54 (d, J 0.7 Hz, 1H), 7.90 (d, J 8.0 Hz, 1H), 7.59−7.52 (m, 2H), 7.20 (ddd, J 8.0, 1.5, 0.8 Hz, 1H), 7.18−7.12 (m, 2H), 7.11 (d, J 1.5 Hz, 1H), 6.11 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.48 (dq, J 17.3, 1.6 Hz, 1H), 5.37 (dq, J 10.5, 1.4 Hz, 1H), 4.74 (dt, J 5.2, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.2, 164.4, and 161.9 (d, $J_{C\text{-}F}$ 248.8 Hz), 161.2, 147.8, 136.2, and 136.1 (d, $J_{C\text{-}F}$ 3.3 Hz), 132.3, 129.02, 128.98, and 128.90 (d, $J_{C\text{-}F}$ 8.3 Hz), 123.9, 119.7, 118.2, 116.0, and 115.8 (d, $J_{C\text{-}F}$ 21.6 Hz), 111.4, 69.3; FTIR (film) v: 3076, 3022, 2925, 2859, 2761, 1683, 1604, 1519, 1488, 1431, 1399, 1277, 1218, 1161, 1013, 996, 930, 901, 821, 691 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{13}FO_2Na$ [M + Na$^+$] 279.0791; Found 279.0793.

Ethyl (*E*)-3-(3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)-acrylate.[33b] Prepared in the same manner as compound **19a**; yield 1.68 g (82%) starting from 1.8 g of 3-(allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-carbaldehyde; white solid, mp 77−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J 16.2 Hz, 1H), 7.57 (d, J 8.0 Hz, 1H), 7.56−7.50 (m, 2H), 7.17−7.09 (m, 3H), 7.05 (d, J 1.6 Hz, 1H), 6.56 (d, J 16.2 Hz, 1H), 6.11 (ddt, J 17.3, 10.6, 5.2 Hz, 1H), 5.46 (dq, J 17.3, 1.7 Hz, 1H), 5.34 (dq, J 10.6, 1.4 Hz, 1H), 4.70 (dt, J 5.2, 1.5 Hz, 2H), 4.27 (q, J 7.1 Hz, 2H), 1.34 (t, J 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.4, 164.0, and 161.5 (d, $J_{C\text{-}F}$ 247.6 Hz), 157.6, 143.3, 139.4, 136.6, and 136.5 (d, $J_{C\text{-}F}$ 3.0 Hz), 132.8, 129.2, 128.7, and 128.6 (d, $J_{C\text{-}F}$ 8.2 Hz), 122.8, 119.6, 118.8, 117.9, 115.9, and 115.7 (d, $J_{C\text{-}F}$ 21.5 Hz), 111.2, 69.4, 60.3, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −114.5; FTIR (film) v: 3073, 3044, 2981, 2955, 2926, 2870, 1709, 1629, 1604, 1520, 1319, 1308, 1264, 1221, 1175, 1161, 1033, 990,817, 676 cm^{-1}; HRMS (ESI-TOF) m/z cald for $C_{20}H_{19}O_3FNa$ [M + Na$^+$] 379.1216; Found 349.1222.

(*E*)-3-(3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)prop-2-en-1-ol (58).[33b] Prepared in the same manner as compound **20a**; yield 541 mg (79%) starting from 780 mg of ethyl (*E*)-3-(3-(allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)acrylate; white solid; mp 83−85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56−7.48 (m, 3H), 7.16−7.08 (m, 3H), 7.02 (d, J 1.7 Hz, 1H), 6.98 (d, J 16.0 Hz, 1H), 6.44 (dt, J 16.0, 5.9 Hz, 1H), 6.11 (ddt, J 17.3, 10.5, 5.2 Hz, 1H), 5.45 (dq, J 17.3, 1.6 Hz, 1H), 5.32 (dq, J 10.5, 1.4 Hz, 1H), 4.65 (dt, J 5.2, 1.5 Hz, 2H), 4.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.7 and 161.3 (d, $J_{C\text{-}F}$ 246.9 Hz), 156.1, 140.8, 137.00, and 136.96 (d, $J_{C\text{-}F}$ 3.2 Hz), 133.2, 129.3, 128.54, and 128.46 (d, $J_{C\text{-}F}$ 8.0 Hz), 127.4, 125.8, 125.1, 119.6, 117.6, 115.7, and 115.5 (d, $J_{C\text{-}F}$ 21.4 Hz), 111.1, 69.3, 64.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.4; FTIR (film) v: 3309, 3242, 2924, 2867, 1602, 1520, 1494, 1423, 1392, 1307, 1222, 1123, 1015, 973, 829 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{17}FO_2Na$ [M + Na$^+$] 307.1110; Found 307.1103.

(*E*)-3-(3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)allyl Carbamate (59). Prepared in the same manner as compound **21a**; yield 910 mg (79%) starting from 1.0 g of allyl alcohol **58**; white solid, mp 137−139 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ: 7.74−7.67 (m, 2H), 7.57 (d, J 8.0 Hz, 1H), 7.26−7.16 (m, 5H), 7.02 (d, J 16.1 Hz, 1H), 6.42 (dt, J 16.1, 6.2 Hz, 1H), 6.14 (ddt, J 17.3, 10.6, 5.1 Hz, 1H), 5.48 (dq, J 17.3, 1.7 Hz, 1H), 5.28 (dq, J 10.6, 1.5 Hz, 1H), 4.74 (dt, J 5.1, 1.6 Hz, 2H), 4.67 (dd, J 6.2, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, acetone-d_6) δ: 163.7 and 161.3 (d, $J_{C\text{-}F}$ 244.8 Hz), 156.2, 140.6, 136.95, and 136.92 (d, $J_{C\text{-}F}$ 3.2 Hz) 133.8, 130.2, 128.7, and 128.6 (d, $J_{C\text{-}F}$ 8.1 Hz), 127.4, 127.1, 125.4, 124.7, 119.2, 116.5, 115.5, and 115.3 (d, $J_{C\text{-}F}$ 21.6 Hz), 111.1, 68.9, 64.7; ^{19}F NMR (376 MHz, acetone-d_6) δ: −117.0; FTIR (film) v: 3428, 3334, 3272, 3210, 2925, 1691, 1604, 1422, 1347, 1222, 830 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{18}FNO_3Na$ [M + Na$^+$] 350.1168; Found 350.1165.

***N*-(1-(3-(Allyloxy)-4′-fluoro-[1,1′-biphenyl]-4-yl)allyl)heptanamide (60).** To a solution of allyl carbamate **59** (300 mg, 0.92 mmol) and Et_3N (560 mg, 770 μL, 5.50 mmol) in dry THF (30 mL) cooled to 0 °C was added TFAA (390 mg, 260 μL, 1.83 mmol), and the resulting mixture was warmed to room temperature slowly. After 1 h, the reaction mixture was cooled to −10 °C and a 2 M soln. of *n*-$C_6H_{11}MgBr$ in Et_2O (2.7 mL, 5.50 mmol) was added dropwise. After stirring at −10 °C for 30 min, the reaction mixture was warmed to room temperature and stirred at that temperature for an additional 2 h. Next, the reaction mixture was poured onto sat. aq. NH_4Cl and extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was chromatographed on silica gel (15% AcOEt in hexanes) to afford 255 mg of **60** (70%) as a white solid; mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52−7.46 (m, 2H), 7.28 (d, J 7.8 Hz, 1H), 7.15−7.08 (m, 3H), 7.03 (d, J 1.6 Hz, 1H), 6.48 (d, J 8.8 Hz, 1H), 6.14−6.01 (m, 2H), 5.84−5.78 (m, 1H), 5.46 (dq, J 17.2, 1.6 Hz, 1H), 5.33 (dq, J 10.6, 1.3 Hz, 1H), 5.18−5.11 (m, 1H), 4.65 (br d, J 5.1 Hz, 2H), 2.22−2.17 (m, 2H), 1.67−1.58 (m, 2H), 1.33−1.24 (m, 6H), 0.89−0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.9, 163.8, and 161.3 (d, $J_{C\text{-}F}$ 246.9 Hz), 156.4, 141.2, 137.7, 136.95, and 136.92 (d, $J_{C\text{-}F}$ 3.1 Hz), 132.9, 129.6, 128.7, and 128.6 (d, $J_{C\text{-}F}$ 8.0 Hz), 127.8, 119.9, 117.8, 115.7, and 115.5 (d, $J_{C\text{-}F}$ 21.4 Hz), 114.8, 111.3, 69.1, 52.9, 37.0, 31.5, 28.9, 25.7, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.3; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{30}FNO_2Na$ [M + Na$^+$] 418.2158; Found 418.2152.

***N*-(8-(4-Fluorophenyl)-2,5-dihydrobenzo[*b*]oxepin-5-yl)-heptanamide (61).** Prepared in the same manner as compound **25a**; yield 160 mg (86%) starting from 200 mg of diene **60**; off-white solid, mp 119−120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54−7.48 (m, 2H), 7.36−7.33 (m, 1H), 7.28−7.24 (m, 2H), 7.15−7.08 (m, 2H), 6.29 (d, J 9.1 Hz, 1H), 6.09−6.02 (m, 1H), 5.63 (ddd, J 11.6, 3.7, 2.0 Hz, 1H), 5.61−5.56 (m, 1H), 4.82−4.75 (m, 1H), 4.51−4.44 (m, 1H), 2.22−2.10 (m, 2H), 1.64−1.57 (m, 2H), 1.30−1.21 (m, 6H), 0.88−0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.8, 162.2, and 159.8 (d, $J_{C\text{-}F}$ 241 Hz), 157.7, 141.6, 136.24, and 136.20 (d, $J_{C\text{-}F}$ 3.5 Hz), 135.2, 129.9, 129.1, 128.6, and 128.5 (d, $J_{C\text{-}F}$ 8.2 Hz), 127.6, 123.2, 120.4, 115.8, and 115.6 (d, $J_{C\text{-}F}$ 21.5), 71.1, 49.0, 36.8, 31.5, 28.8, 25.5, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.2; FTIR (film) v: 3279, 2954, 2928, 1644, 1519, 1491 cm^{-1}; HRMS (ESI-TOF): m/z calcd for $C_{23}H_{26}FNO_2Na$ [M + Na$^+$] 390.1845; Found 390.1854.

***N*-(8-(4-Fluorophenyl)-2,3,4,5-tetrahydrobenzo[*b*]oxepin-5-yl)heptanamide (62).** To a solution of oxepine **61** (150 mg, 0.42 mmol) in 30 mL of AcOEt was added 10 mg of 10% Pd/C, and the resulting mixture was saturated with hydrogen. After 3 h, the reaction mixture was diluted with AcOEt and filtered through a Celite pad. Removal of the solvent gave 145 mg (96%) of product **62** as a white solid. mp 132−133 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.21 (d, J 8.3 Hz, 1H), 7.66 (dd, J 8.6, 5.6 Hz, 2H), 7.31−7.19 (m, 5H), 5.05 (td, J 8.8, 2.7 Hz, 1H), 4.17 (dt, J 12.0, 4.5 Hz, 1H), 3.78 (dt, J 12.0, 7.2, 4.4 Hz, 1H), 2.18 (t, J 7.4 Hz, 2H), 1.97−1.90 (m, 2H), 1.85−1.72 (m, 2H), 1.55−1.47 (m, 2H), 1.30−1.20 (m, 6H), 0.84 (t, J 6.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.1, 163.8, and 161.3 (d, $J_{C\text{-}F}$ 246.7 Hz), 159.8, 141.3, 136.15, and 136.11 (d, $J_{C\text{-}F}$ 3.1 Hz), 133.8, 130.1, 128.54, and 128.46 (d, $J_{C\text{-}F}$ 8.0 Hz), 122.6, 120.6, 115.8, and 115.5 (d, $J_{C\text{-}F}$ 21.5 Hz), 74.1, 52.2, 36.9, 31.5, 30.3, 28.9, 26.7, 25.7, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.2; FTIR (film) v: 3281, 3063, 2953, 2929, 2857, 1644, 1538, 1519, 1490, 1234, 1207, 1159, 841, 818 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{28}FNO_2Na$ [M + Na$^+$] 392.2002; Found 392.2003.

3-(2,4-Difluorophenyl)-1-(8-(4-fluorophenyl)-2,3,4,5-tetrahydrobenzo[*b*]oxepin-5-yl)-1-heptylurea (16).[24] To a solution of amide **62** (45 mg, 0.12 mmol) in 10 mL of dry THF was added a 2 M soln. of $LiAlH_4$ in THF (0.32 mmol, 160 μL), and the mixture was refluxed overnight. Next, the reaction mixture was diluted with Et_2O (30 mL) and sat. Na_2SO_4 (200 μL) was added. The solid was removed by filtration, and the organic solution was dried over anhydrous Na_2SO_4. After removal of solvents, the crude amine **63** was dissolved in 5 mL of dry THF and 2,4-difluorophenyl isocyanate (0.14 mmol, 21 mg, 16 μL) was added slowly. After 4 h, water was added and the resulting mixture was extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4. After removal of solvents, the crude product was chromatographed on silica gel (20% AcOEt in hexanes) to afford 42 mg (73%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (td, J 9.1, 5.9 Hz, 1H), 7.52−7.49 (m, 1H), 7.45 (dd, J 8.8, 5.3 Hz, 1H), 7.37−7.33 (m, 1H), 7.28−7.23 (m, 1H), 7.19−7.16 (m, 1H), 7.14−7.10 (m, 1H), 7.03 (t, J 8.7 Hz, 1H), 6.79−6.70

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(m, 2H), 6.42 (s, 1H), 5.29−5.23 (m, 1H), 4.24−4.16 (m, 1H), 3.89−3.82 (m, 1H), 3.41−3.31 (m, 1H), 3.28−3.19 (m, 1H), 2.21−2.11 (m, 2H), 2.01−1.92 (m, 2H), 1.61−1.51 (m, 2H), 1.25−1.13 (m, 8H), 0.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.6 and 161.6 (d, J 246.8 Hz), 158.50, 158.45, 158.8, 158.7, 156.8, and 156.7 (dd, J 244.7, 11.5 Hz), 154.71, 154.69, 153.6, 153.5, 151.6, and 151.5 (dd, J 244.0, 11.7 Hz), 142.0, 141.0, 139.9, 136.1, and 136.0 (d, J 3.1 Hz), 131.5, 131.4, 128.8, 128.51, and 128.45 (d, J 8.0 Hz), 127.5, 126.9, 123.91, 123.88, 123.83, and 123.80 (dd, J 10.1, 3.6 Hz), 122.8 and 122.7 (d, J 8.9 Hz), 122.6, 122.4, 120.8, 120.7, 115.7, and 115.6 (d, J 21.5 Hz), 111.08, 111.05, 110.90, and 110.88 (dd, J 21.7, 3.5 Hz), 103.4, 103.18, 103.16, and 103.0 (dd, J 26.7, 23.6 Hz), 72.4, 58.9, 46.8, 31.7, 30.9, 30.1, 28.9, 28.2, 27.2, 22.5, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −115.2, −117.6 (d, J 18.5 Hz), −127.9 (d, J 18.5 Hz); FTIR (film) ν: 3467, 3314, 3060, 3033, 2934, 2928, 2857, 1665, 1611, 1520, 1487, 1429, 1304, 1255, 1196, 1140, 966, 845, 762 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{30}H_{33}N_2O_2F_3K$ [M + K$^+$] 549.2131; Found 549.2128.

1-(2-(Allyloxy)-4-chlorophenyl)prop-2-en-1-amine (64). To a solution of allyl carbamate **21f** (150 mg, 0.56 mmol) and Et_3N (342 mg, 470 μL, 3.36 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (237 mg, 157 μL, 1.12 mmol), and the resulting mixture was warmed to room temperature slowly. In a separate flask, a 1 M soln. of LiHMDS in THF (3.4 mL, 3.36 mmol) was added to a solution of TMSOH (400 μL) in dry THF (5 mL). After 1 h, the solution of TMSOLi was added to the generated allyl isocyanate, and the reaction mixture was stirred for 4 h. Next, a 1 M soln. of TBAF (4 mmol, 4 mL) was added and the resulting mixture was trirred overnight. Then, the volatiles and solvent were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (20% to 60% AcOEt in hexanes) to afford 92 mg of amine **64** (73%) as a yellowish oil; ^{1}H NMR (400 MHz, C_6D_6) δ: 7.06 (d, J 8.2 Hz, 1H), 6.82 (dd, J 8.2, 2.0 Hz, 1H), 6.60 (d, J 2.0 Hz, 1H), 5.93 (ddd, J 17.2, 10.3, 5.5 Hz, 1H), 5.60 (ddt, J 17.3, 10.4, 5.0 Hz, 1H), 5.17 (dt, J 17.2, 1.7 Hz, 1H), 5.09 (dq, J 17.3, 1.7 Hz, 1H), 4.98−4.93 (m, 2H), 4.72 (d, J 5.6 Hz, 1H), 3.85−3.80 (m, 2H); ^{13}C NMR (101 MHz, C_6D_6) δ: 156.2, 141.1, 133.0, 132.6, 132.1, 128.2, 120.8, 116.8, 113.1, 112.4, 68.4, 51.9; MS (ESI-TOF) m/z 207.1 [(M − NH_2)$^+$](86%), 224.6 [M + H$^+$] (7%).

***N*^{2},*N*^{3}-Di-Boc-1-(1-(2-(allyloxy)-4-chlorophenyl)allyl)-guanidine (66).** A solution of amine **64** (90 mg, 0.4 mmol) and *N*,*N*′-di-Boc-1*H*-pyrazole-1-carboxyamide (65, 187 mg, 0.6 mmol) in 4 mL of dry DMF was stirred overnight. Next, the reaction mixture was poured into the water and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography on silica gel (5% to 10% AcOEt in hexanes) to afford 135 mg (72%) of guanidine derivative **66** as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.49 (s, 1H), 9.22 (d, J 8.5 Hz, 1H), 7.19 (d, J 8.1 Hz, 1H), 6.90 (dd, J 8.1, 2.0 Hz, 1H), 6.86 (d, J 2.0 Hz, 1H), 6.14−5.96 (m, 3H), 5.41 (dq, J 17.3, 1.6 Hz, 1H), 5.27 (dq, J 10.6, 1.4 Hz, 1H), 5.14−5.07 (m, 2H), 4.65−4.54 (m, 2H), 1.48 (s, 9H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.7, 156.7, 155.3, 153.0, 136.9, 134.1, 132.6, 130.0, 127.1, 120.8, 117.9, 114.9, 113.1, 82.8, 79.0, 69.4, 53.1, 28.3, 28.1; FTIR (film) ν: 3322, 3276, 3087, 2979, 2932, 1772, 1637, 1613, 1566, 1489, 1409, 1237, 1325, 1248, 1229, 1155, 1123, 1057, 809 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{33}N_3O_5Cl$ [M + H$^+$] 466.2109; Found 466.2102.

***N*^{2},*N*^{3}-Di-Boc-1-(8-chloro-2,5-dihydrobenzo[*b*]oxepin-5-yl)-guanidine (67).** Prepared in the same manner as compound **25a**; yield 51 mg (77%) starting from 70 mg of diene **66**. Two portions of Grubbs II catalysts were applied (2 × 5 mg, second portion of catalyst was added after 2 h; overall reaction time 4 h); low melting solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.43 (s, 1H), 9.00 (d, J 7.9 Hz, 1H), 7.24 (d, J 8.1 Hz, 1H), 7.11 (d, J 2.2 Hz, 1H), 7.06 (dd, J 8.1, 2.2 Hz, 1H), 6.00−5.93 (m, 2H), 5.61−5.55 (m, 1H), 4.74−4.67 (m, 1H), 4.51−4.45 (m, 1H), 1.49 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.6, 158.0, 155.1, 152.9, 134.9, 133.9, 129.7, 128.7, 127.5, 124.6, 122.6, 83.1, 79.2, 71.0, 49.2, 28.3, 28.1; FTIR (film) ν: 3321, 3114, 2979, 1722, 1638, 1612, 1555, 1479, 1413, 1368, 1334, 1316, 1227, 1155, 1119, 1057 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{29}N_3O_5Cl$ [M + H$^+$] 438.1796; Found 438.1790.

***N*^{2},*N*^{3}-Di-Boc-1-(8-chloro-2,3,4,5-tetrahydrobenzo[*b*]oxepin-5-yl)guanidine (68).** A solution of **67** (40 mg, 0.092 mmol) in 3 mL of AcOEt was added to a suspension of $Pd(OH)_2$ (10 mg) in AcOEt, and the resulting mixture was saturated with hydrogen for 1.5 h. Next, a catalyst was removed by filtration through a Celite pad and solvent was removed. The crude product was purified by flash column chromatography on silica gel to afford 34 mg (88%) of guanidine derivative **68** as a white solid. mp 168−170 °C (Lit.[33b] 169−171 °C); spectral data in accordance with the literature.[33b] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.45 (s, 1H), 8.99 (d, J 8.7 Hz, 1H), 7.25−7.22 (m, 1H), 7.06−7.03 (m, 1H), 7.03−6.99 (m, 1H), 5.52−5.46 (m, 1H), 4.31 (d, J 12.3 Hz, 1H), 3.85−3.75 (m, 1H), 2.25−2.12 (m, 2H), 1.93−1.70 (m, 2H), 1.49 (s, 9H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.7, 160.3, 155.1, 153.0, 133.8, 133.1, 130.4, 124.0, 122.7, 83.1, 79.2, 73.9, 52.5, 30.4, 28.3, 28.1, 26.9; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{31}N_3O_5Cl$ [M + H$^+$] 440.1952; Found 440.1947.

Benzyl (1-(2-(Allyloxy)-4-chlorophenyl)allyl)carbamate (69). Prepared in the same manner as compound **24p**; yield 375 mg (93%) starting from 300 mg of carbamate **21f**; waxy solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.91 (d, J 9.0 Hz, 1H), 7.37−7.25 (m, 6H), 7.03 (d, J 2.0 Hz, 1H), 6.98 (dd, J 8.2, 2.1 Hz, 1H), 6.07−5.93 (m, 1H), 5.92−5.83 (m, 1H), 5.60−5.54 (m, 1H), 5.43−5.35 (m, 1H), 5.27−5.21 (m, 1H), 5.08−4.96 (m, 4H), 4.61 (d, J 5.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.5, 155.6, 139.2, 137.3, 136.6, 134.1, 132.3, 129.5, 128.5, 128.1, 127.7, 121.0, 118.1, 115.2, 113.1, 69.2, 66.8, 54.1; FTIR (film) ν: 3438, 3331, 3087, 3066, 3032, 2983, 2928, 1710, 1595, 1489, 1408, 1244, 1092, 1024, 998, 927, 897, 698 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{20}ClNO_3Na$ [M + Na$^+$] 380.1029; Found 380.1032.

Benzyl (8-Chloro-2,5-dihydrobenzo[*b*]oxepin-5-yl)carbamate (70). Prepared in the same manner as compound **25a**; yield 110 mg (64%) starting from 185 mg of diene **69**; white solid, mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38−7.27 (m, 5H), 7.23−7.04 (m, 3H), 6.03−5.95 (m, 1H), 5.63−5.54 (m, 2H), 5.32−5.23 (m, 1H), 5.12 (br d, J 12.0 Hz, 1H), 5.02 (br d, J 12.0 Hz, 1H), 4.67 (br d, J 17.6 Hz, 1H), 4.44 (br d, J 17.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.7, 155.4, 136.3, 135.2, 134.0, 129.8, 128.9, 128.5, 128.15, 128.13, 127.3, 124.8, 122.6, 71.0, 66.9, 50.9; FTIR (film) ν: 3419, 3325, 3064, 3031, 2939, 2892, 2852, 1705, 1597, 1482, 1317, 1268, 1221, 1075, 1038, 1001, 875, 737, 697, 615 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}ClNO_3Na$ [M + Na$^+$] 352.0716; Found 352.0715.

Compound 76.[47] To a solution of allyl carbamate (*S*)-**42** (30 mg, 0.12 mmol) and Et_3N (75 mg, 101 μL, 0,73 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (52 mg, 35 μL, 0.24 mmol), and the resulting mixture was warmed to room temperature slowly. In separate flask, Et_3N (50 μL) was added to a solution of (*R*)-*N*-(4-chlorobenzyl)-*N*-methylpyrrolidine-2-carboxamide hydrochloride (**74**)(40 mg, 0.13 mmol)[47] in 5 mL of dry THF. When the rearrangement reaction was completed, volatiles and solvent were removed under diminished pressure and the residue was dissolved in 5 mL of dry THF. The obtained solution was added to a solution of proline derivative **74**. After stirring overnight, solvents were removed and residue was purified by flash chromatography on silica gel (15% to 60% AcOEt in hexanes) to provide 38 mg (65%) of product **75**, which was directly used in the next step. HRMS (ESI-TOF) m/z calcd for $C_{27}H_{33}N_3O_3Cl$ [M + H$^+$] 482.2210; Found 482.2206. A solution of compound **75** (38 mg, 0.08 mmol) in 10 mL of degassed DCE was added to a solution of Grubbs II catalyst (3.3 mg, 3.9 μmol) in 1 mL of degassed DCE, and the resulting mixture was kept at 55 °C for 1.5 h. Then, solvent was removed and the residue was purified by flash chromatography on silica gel (25 to 75% AcOEt in hexanes) to afford 26 mg (76%) of compound **76** as a low melting solid; $[\alpha]_D^{21}$ +6.9 (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, DMSO-d_6, mixture of rotamers) δ: 7.48−7.10 (m, 8H), 6.79 (d, J 8.9 Hz, 1H), 6.11−6.02 (m, 1H), 5.86−5.81 (m, 1H), 5.52 (dq, J 11.7, 2.8 Hz, 1H), 4.87−4.77 (m, 2H), 4.59 (d, J 15.1 Hz, 1H), 4.51 (d, J 15.1 Hz, 1H), 4.38 (dq, J 17.4, 2.7 Hz, 1H), 3.59 (t, J 6.9 Hz, 2H), 3.39 (s, 3H), 2.29−2.22 (m, 1H), 2.07−

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1.94 (m, 2H), 1.86−1.74 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6, mixture of rotamers) δ: 173.1, 156.7, 155.8, 139.8, 137.2, 137.0, 134.9, 132.2, 132.0, 131.9, 131.9, 129.7, 129.6, 129.4, 128.9, 128.8, 128.4, 128.4, 127.9, 126.8, 125.1, 125.0, 124.2, 124.2, 121.7, 121.7, 71.0, 57.0, 56.7, 51.8, 50.1, 48.7, 46.4, 34.9, 31.6, 30.3, 27.0; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{26}N_3O_3ClNa$ [M + Na$^+$] 462.1560; Found 462.1546.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01691.

Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra and HPLC for selected compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sebastian.stecko@icho.edu.pl.

Notes

The authors declare no competing financial interest.

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