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The Synthesis of Chiral β,β-Diaryl Allylic Alcohols and Their Use in the Preparation of α-Tertiary Allylamines and Quaternary α-Amino Acids

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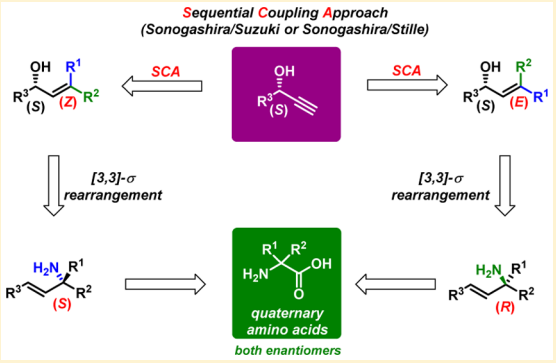
Supporting Information

ABSTRACT: An approach to nonracemic β,β-diarylsubstituted allyl alcohols is described. Their synthesis starts from L-lactic acid-derived propargyl alcohol, which is submitted to sequential Sonogashira/Suzuki or Sonagashira/Stille coupling reactions. Both approaches enable the synthesis of either (*Z*)- or (*E*)-allylic alcohols regarding the order of introducing coupling agents. The obtained allyl alcohols were applied in the synthesis of nonracemic α-tertiary allylamines via stereocontrolled cyanate-to-isocyanate sigmatropic rearrangement reactions of the corresponding allyl carbamates. The stereoselectivity of the process is controlled by the geometry of the double bond of the starting allyl derivative. As demonstrated, a rearrangement of (*S*,*Z*)-allyl carbamates provides (*S*)-teriary allylamines, whereas the transformation (*S*,*E*)-isomers leads to (*R*)-allylamines.



INTRODUCTION

These days, the synthesis of tertiary stereogenic centers, that is, carbon atoms bearing one hydrogen atom and three different substituents, can be achieved easily in most cases through a myriad of synthetic approaches by using either a chiral auxiliary, reagent, or catalyst. At the same time, the related approaches to organic molecules bearing quaternary stereocenters are still challenging to synthetic organic chemists. As a result, every stereocontrolled procedure for the generation of a fully substituted carbon atom stereocenter is of great value. Right after chiral tertiary alcohols, chiral tertiary amines are the next most frequently occurring in nature class of organic molecules bearing a heteroatom-substituted quaternary center. Natural or synthetic compounds of this class display a wide spectrum of biological activities (Figure 1). Moreover, they are also highly attractive building blocks for organic synthesis. Particularly interesting are allylamines bearing an amino function bonded to a quaternary carbon atom as these can serve as attractive precursors of various classes of biomolecules, including unnatural quaternary α-amino acids.[1]

The enantioselective synthesis of α-tertiary allylamines remains a synthetic challenge.[1−3] The most common approaches to these compounds involve nucleophilic addition to ketimines.[2,4−6] However, these methods are still limited due to the low reactivity of these species as well as the difficulty of achieving good stereoselectivity. An interesting but less explored approach is the synthesis of chiral tertiary amines via sigmatropic rearrangement reactions (Scheme 1)[7] such as the Overman rearrangement,[8] the Ichikawa reaction,[5c,9,10] or other reactions.[11] Although such an intramolecular approach to the synthesis of the C−N bond is highly attractive, it is limited by the availability of the required nonracemic starting materials, the corresponding β,β-disubstituted allylic alcohols with both high enantio- and (*E*/*Z*)-purity (Scheme 1).

Such trisubstituted alkenes are common structural motifs in nature. They are also useful building blocks in synthesis and can, for instance, be enantioselectively hydrogenated[12] or isomerized to the corresponding nonracemic aldehydes or ketones.[13] Unfortunately, stereocontrolled synthesis of chiral β,β-disubstituted allyl alcohols remains a challenge. Most common approaches are based on asymmetric reduction of enones[13f,14,15] or enantioselelective addition to enals (Scheme 2).[9b,16] Other methods involve vinylation of aldehydes,[6a−d] olefination of hydroxy aldehydes,[8c,e] or by kinetic resolution processes.[17] However, these methods lack generality and very often suffer from insufficient efficiency and stereoselectivity. In addition, enones or enals often are contaminated by *E* or *Z* isomers resulting from imperfect selectivity of olefination reactions commonly used as the method for their preparation. The starting materials for the sigmatropic rearrangement must display very high *E*/*Z* purity; otherwise, they afford the corresponding allylamine product with lower enantioenrichment.

Looking for an efficient method for the preparation of allyl alcohols of type **1** and **2** (Scheme 2), we turned our attention to the chiral pool approach. As outlined in Scheme 2, these compounds were planned to be synthesized starting from the corresponding chiral propargyl-type alcohols, which we intended to subject to sequential coupling processes.

Herein, we report the first part of our studies that concern the preparation of both β,β-diaryl (*Z*)- and (*E*)-allylic alcohols

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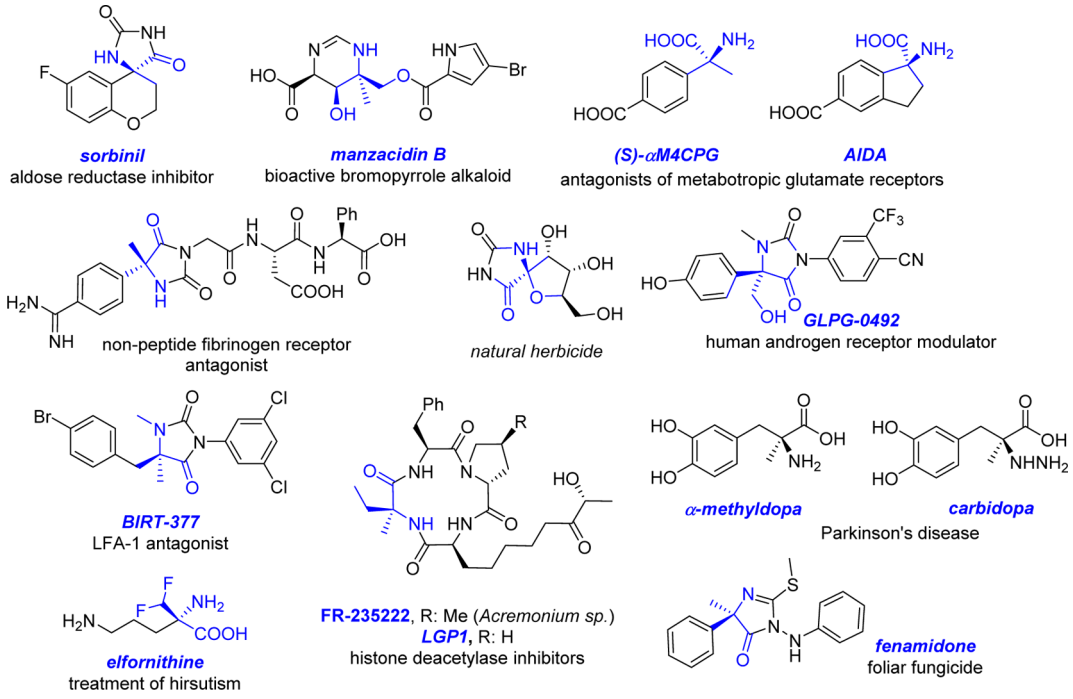
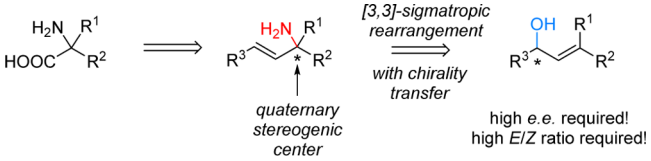
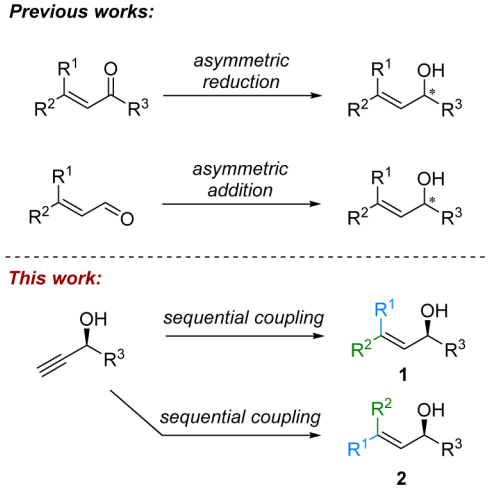


Figure 1. Bioactive chiral teriary amines and their derivatives.

Scheme 1. An Approach to Quaternary Amino Acids via [3,3]-Sigmatropic Rearrangement

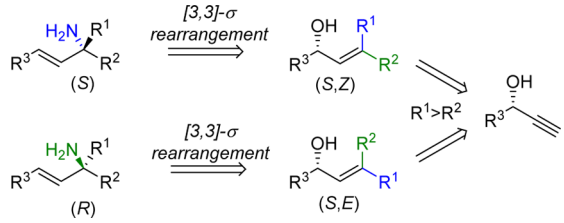


Scheme 2. Synthesis of β,β-Disubstituted Allyl Alcohols



(**1** and **2**) bearing the same configuration at the stereogenic center. After further *O*-functionalization, these alcohols should rearrange to either (*S*)- or (*R*)-α-tertiary-allylamines with complete chirality transfer due to a concerted mechanism of a sigmatropic process. In contrast to the typical approach,[8−10] the stereochemical outcome in this case will not be governed by a configuration of the stereogenic center but rather by a configuration of the double bond (Scheme 3).

Scheme 3. Double Bond-Controlled Enantiospecific Synthesis of Tertiary-α-allylamines



RESULTS AND DISCUSSION

The commercially available (*S*)-3-butyn-2-ol (**3**, 97% ee) was coupled with PhI in the presence of a palladium catalyst to afford **4a** in 97% yield (Scheme 4).

In the next step, propargyl alcohol **4a** was treated with 2.2 equiv of Red-Al. The hydroaluminated product was directly quenched with I_2 in THF to provide the corresponding halodemetalation product **5a** in 90% yield (Scheme 4). The analogous vinyl bromide (**5b**) was obtained in comparable yield (92%). Bromide **5b** proved to be more stable and easier to handle than iodide **5a**; therefore, it was applied in further steps. The hydroalumination/bromination sequence also proceeded smoothly for both 4-tolyl- and 4-fluorophenyl-substituted propargyl alcohols. However, it failed in the case of *p*-methoxyphenyl-substituted starting material, which we presume was too electron-rich to withstand the conditions of the bromination step. To overcome this problem, we modified the electronic properties of the phenyl ring in **4c** by replacing the methyl group with Ts (**4e**).[18] Now, the hydroalumination/bromination proceeded readily, affording desired bromide **5f** in 92% yield (Scheme 4).

With vinyl bromides **5a−f** in hand, we began studies on the introduction of a second aryl ring via the Suzuki coupling reaction with arylboronic acids. In a model reaction, vinyl

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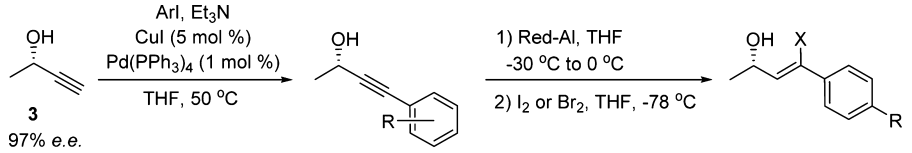
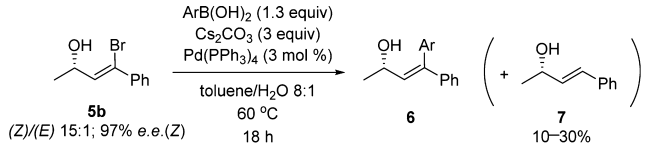
Scheme 4. Synthesis of Vinyl Halides 5

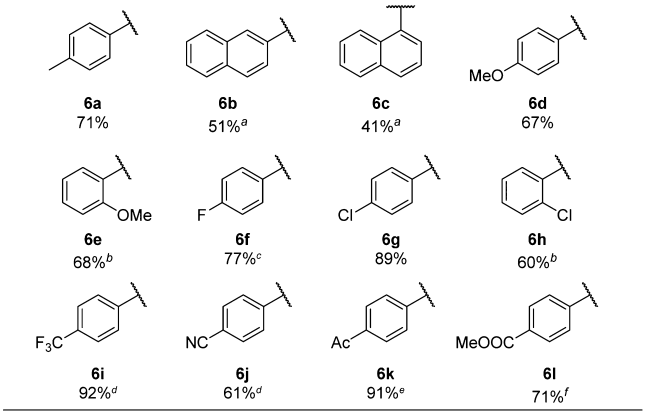


4a R: H, 97%
4b R: 4-Me, 95%
4c R: 4-OMe, 97%
4d R: 4-F, 97%
4e R: 4-OTs, 95%
4f R: 2-OMe, 94%
4g R: 2-Cl, 97%
4h Ar: 1-naphtyl, 91%
4i Ar: 2-naphtyl, 97%

5a R: H, X: I, 90%
5b R: H, X: Br, 92%, Z/E 15:1
5c R: 4-Me, X: Br, 85%, Z/E 10:1
5d R: 4-F, X: Br, 82%, Z/E 15:1
5e R: 4-OMe, X: Br, 0%
5f R: 4-OTs, X: Br, 92%, Z/E 35:1

Scheme 5. Synthesis of (*S*,*Z*)-Allyl Alcohols 6 via Suzuki Coupling





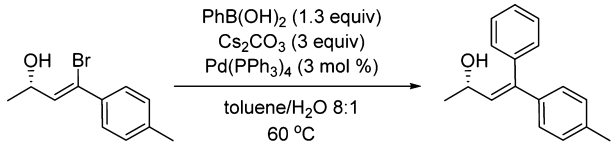
[a]Yield after 24 h (low conversion). [b]Yield after 30 h. [c]*Z*/*E* ratio of 27:1 (NMR). [d]Only (*Z*) isomer. [e]*Z*/*E* ratio of 16:1 (NMR). [f]*Z*/*E* ratio of 20:1 (NMR).

bromide **5b** was subjected to the reaction with *p*-tolylboronic acid in the presence of 3 mol % $Pd(PPh_3)_4$ and Cs_2CO_3 as a base (Scheme 5). The reaction was performed in a toluene/water mixture (8:1), which was the optimal solvent system (for optimization, see the Supporting Information (SI)). Under these conditions, *β*,*β*-diaryl-substituted allyl alcohol **6a**, as well as its analogues **6b**–**l**, were prepared in moderate-to-good yields (Scheme 5). Unfortunately, the major products were accompanied by a small amount of compound **7** (10–30%), which was probably the result of a side debromination process. The optimization of reactions conditions minimized but did not eliminate its formation.

The reverse order of introduction of the aryl groups enabled the preparation of isomeric allyl alcohols, for instance, compound **8a**, which was prepared through the coupling of vinyl bromide **5c** with phenylboronic acid (Scheme 6).

Although the coupling reaction proceeded well for *p*-substituted boronic acids, the same process involving *o*-substituted ones proceeded slower and with low conversion after the standard reaction time (20 h). The same issue was

Scheme 6. Synthesis of (*S*,*E*)-Allyl Alcohols 8 via Suzuki Coupling



noted in the case of the coupling reaction of bromide **5b** with 1- and 2-naphthylboronic acids. In both cases, extension of the reaction times was required to achieve complete conversion of the starting material. At the same time, the overall yield dropped significantly. One of the reasons for this was the thermal decomposition of the starting bromide as well as self-coupling of boronic acid. Because of the sluggish course of the desired coupling reaction, the side debromination process of initial vinyl bromide was more favored, which resulted in increased formation of product **7** (>50%). Despite many attempts at changing the reaction conditions or the catalytic system, this side process could not be eliminated.

With chiral *β*,*β*-disubstituted allyl alcohols in hand, we began the studies on their transformation into the corresponding allylamines via an oxygen-to-nitrogen [3,3]-sigmatropic rearrangement process. As the method of choice, we selected the Ichikawa cyanate-to-isocyanate rearrangement (Scheme 7)[8a,17] as a rapid and straightforward method for the transformation of allyl alcohols into the corresponding allylamines. This reaction proceeded under mild conditions and without the use of any metal catalysts.[8a,17] The concerted mechanism of the reaction guarantees high [1,3]-chirality transfer to the newly formed stereogenic center.[8a,17] Moreover, smooth direct functionalization of the isocyanate intermediate with various nucleophiles enables the formation of allylamine derivatives such as amides, carbamates, or ureas in a one-pot reaction sequence.[9a,19,20]

Thus, the treatment of allyl alcohol **6a** with trichloroacetyl isocyanate (TCAI), followed by hydrolysis in an aq K_2CO_3/MeOH mixture gave allyl carbamate **9a** in 73% overall yield (Scheme 8). Next, carbamate **9a** was dehydrated by the use of TFAA in the presence of Et_3N to form an allyl cyanate, which then spontaneously rearranged to the corresponding allyl isocyanate (compare with Scheme 7). The isocyanate was not isolated but directly trapped by treatment with MeOH in the presence of a catalytic amount of Bu_3SnOMe[21] (10 mol %) to provide allyl carbamate **10a** enantiospecifically in 78% overall

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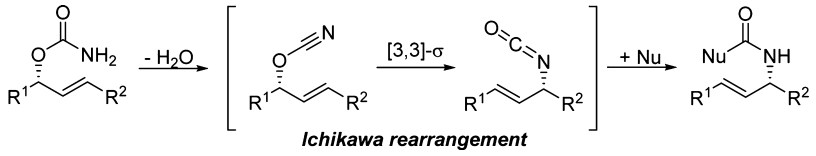
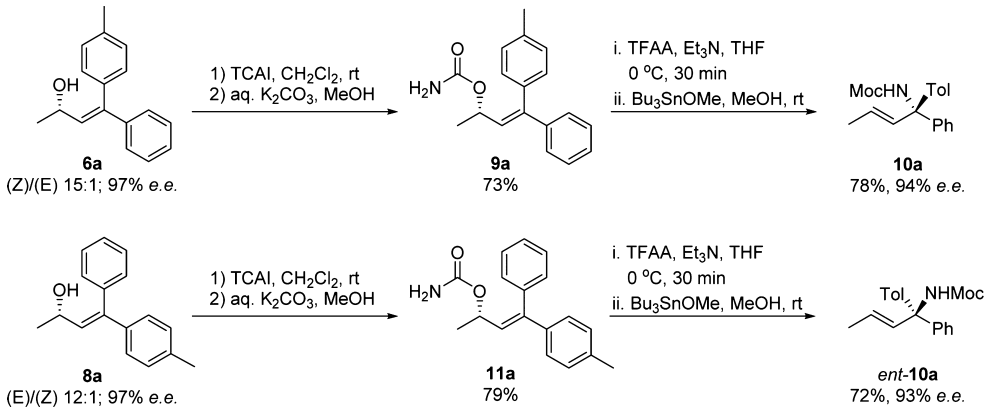
Scheme 7. Ichikawa [3,3]-Sigmatropic Rearrangement



Scheme 8. Synthesis of Allylamines 10 and *ent*-10a



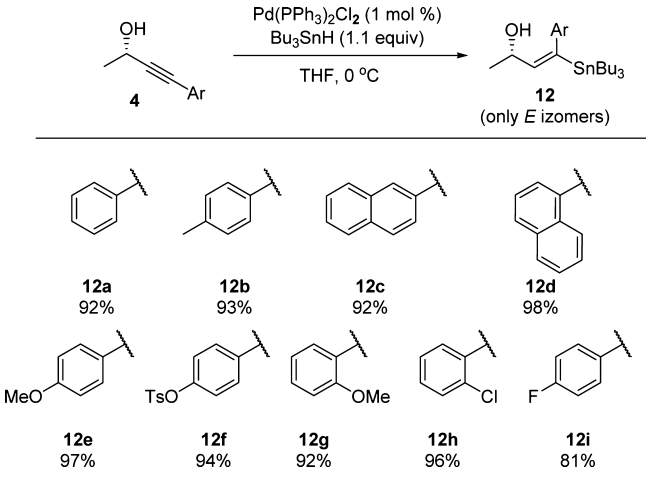
yield after 3 steps. In the same manner, allyl alcohol **8a** was transformed into carbamate **11a**, and this compound was next subjected to the dehydration/rearrangement/addition process to provide the enantiomeric allyl carbamate *ent*-**10a** (Scheme 7).

Surprisingly, the comparison of HPLC data of **10a** and *ent*-**10a** with a chromatogram of a racemic sample showed that both allylamines had slightly lower enantiopurities (Scheme 8) than that of starting propargyl alcohol **3** (97% ee). The same problem was also noted for other allyl alcohols.

Careful examination of NMR spectra of vinyl bromides **5b–d** and **5f** revealed the presence of small amounts of their geometric isomers (according to integration of vinyl protons). The *Z*/*E* ratio was in the range of 10:1 to 35:1, giving 3–9% contamination of the main *Z*-product by the *E*-isomer. Unfortunately, these unwanted isomers were hard to remove by chromatography from the desired *Z*-vinyl bromides. The contamination of *Z*-bromide with its *E*-isomer has a significant influence on the enantiopurity of the desired allylamines. For example, assuming that *Z*/*E* and ee in further steps do not change, the transformation of *Z*-vinyl bromide (with 97% ee) containing 5% of the *E*-isomer should provide the corresponding allylamine with only ~92% ee. To make matters worse, after Suzuki coupling, isomeric *E*/*Z* allylic alcohols are completely inseparable. The situation is even more complicated in the case of electron-rich allylic alcohols because of a theoretically possible partial racemization in the presence of an excess of boronic acid during the coupling, which cannot be precluded.

These inconveniences forced us to reconsider our synthetic strategy and to propose an alternative approach for the preparation of the desired chiral *β*,*β*-disubstituted allyl alcohols that would bypass the previously described problems. Because vinylstannanes are known to be highly valuable reagents in alkene synthesis,[22] particularly via the Stille reaction,[19d,20] we decided to transform the alkynols **4a–i** to the corresponding vinylstannanes **12a–i**. The hydrostannylation was performed by the treatment of alkynes with Bu_3SnH in the presence of 1 mol % $Pd(PPh_3)_2Cl_2$ (Scheme 9), according to a report by Organ and others,[23] and provided the corresponding *β*-

Scheme 9. Synthesis of Vinyl Stannanes 12



vinylstannanes in good yields. These products were obtained stereoselectively, and *Z*-isomers were not detected by NMR (lack of additional vinyl proton). Vinyl stannanes **12** were accompanied by minor amounts of the regioisomeric *α*-vinylstannanes, but it was not a problem because they could be easily chromatographically separated from the major products. Additionally, it was found that, to achieve a high yield of the process, the starting material cannot contain any copper impurities from the previous step. Therefore, alkynols **4** were distilled prior to the hydrostannylation.

With vinylstannanes **12** in hand, an investigation of the scope and limitations of the Stille coupling reaction with various aryl iodides was undertaken. As shown in Scheme 10, the coupling process proceeded efficiently to provide the desired nonracemic *β*,*β*-disubstituted allyl alcohols **8** with no loss of enantiopurity noted. As in the case of the Suzuki reaction, under standard conditions, the Stille coupling with 2-substituted aryl iodides was again slower, and low conversion of the starting material was observed after the standard reaction time (18h). For this reason, the syntheses of **8d** and **8h** required an extension of the

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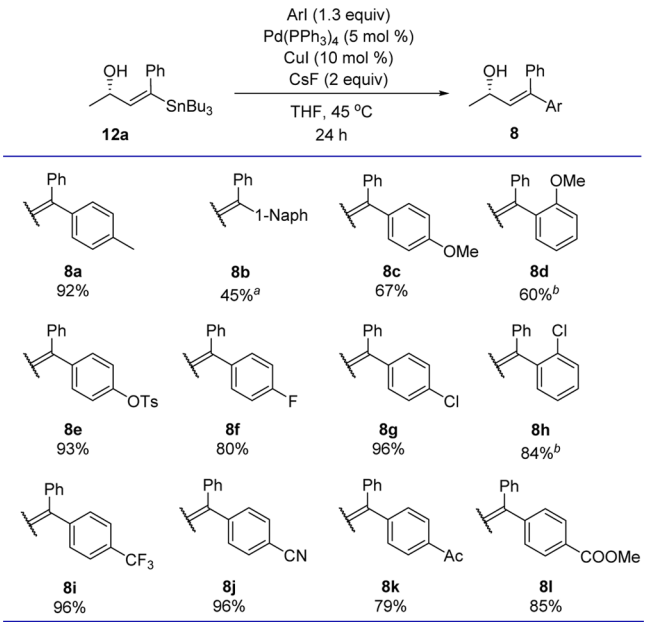
Scheme 10. Synthesis of (*S*,*E*)-Allyl Alcohols 8 via Stille Coupling

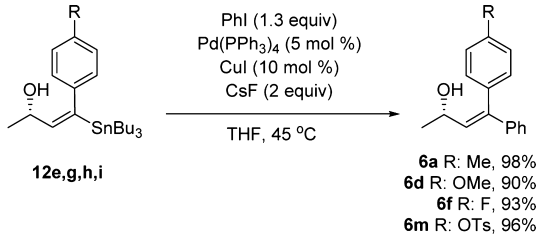


[a]After 3 days (54% conversion). [b]Reaction time extended to 48 h to achieve full conversion of the starting material.

reaction time. The efficiency of the coupling process was dramatically reduced in the case of the reaction of **8b** with 1-iodonaphtalene. After the standard reaction time (20 h), low conversion of the starting material was noted. This result as well as previous studies on the Suzuki coupling indicate that, regardless of the manner of introduction of the second aryl group, this process is highly sensitive to steric effects (compare with Scheme 5).

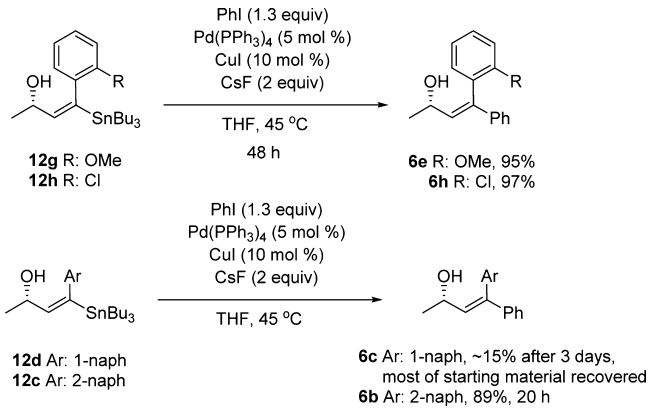
In the same manner, a second set of allyl alcohols with the same configuration at the stereogenic center but opposite geometry of the double bond (**6a**, **6d**, **6f**, and **6m**) were

Scheme 11. Synthesis of (*S*,*Z*)-Allyl Alcohols 6 via Stille Coupling



synthesized (Scheme 11) by coupling with iodobenzene. For all vinylstannanes with a 4-substituted phenyl ring (**12b**–**e**), the reaction proceeded efficiently to afford the desired products. In the case of vinylstannanes bearing a 2-substituted phenyl ring (**12g** and **12h**), the coupling was much slower, probably because of steric effects. Ultimately, for complete conversion of the starting material to be achieved (Scheme 12), extension of the reaction time to 48 h was required. Unfavorable steric effects are particularly visible in the case of 1-naphthyl-substituted vinylstannane **12d**, which was highly inert in the investigated process. After 3 days of reaction time, less than 15% of desired product **6c** was isolated along with unreacted

Scheme 12. Synthesis of Allyl Alcohols 6b, 6c, 6e, and 6h via Stille Coupling



starting material and some byproducts (Scheme 12). The change in the reaction conditions, for instance, increasing the reaction temperature above 90 °C and changing the catalytic system, did not facilitate the coupling process. Most likely, the presence of the cumbersome group in the vicinity of the double bond in the vinylstannane strongly interferes with the transmetalation step with the palladium-bound aryl iodide and results in low conversion of this starting material. The analogous coupling reaction of iodobenzene with vinyl stannane **12c** with a 2-naphtyl ring can test this hypothesis (Scheme 12). In this case, the reaction proceeded efficiently and provided the desired allyl alcohol **6b** in good yield (89%) after 20 h (Scheme 12).

Next, with both series of isomeric chiral *β*,*β*-disubstituted allyl alcohols in hand, we could again begin the investigation on their transformation into the corresponding allylamines by cyanate-to-isocyanate rearrangement. Allyl alcohols **6** were transformed into the corresponding (*S*,*Z*)-allyl carbamates **9** and subjected to the rearrangement reaction, as shown in Scheme 13. The rearrangement proceeded well in all cases to provide the desired tertiary (*S*)-allylamines **10** in overall yields above 70% after 3 steps. One exception was the case when allyl carbamates bearing a MeO-substituted phenyl ring were applied. These substrates decomposed rapidly during the reaction course and gave a very poor yield of the desired products. Fortunately, a convenient solution was the replacement of the OMe group in alcohol **8c** by OTs (**8e**), as was done previously in the case of hydroalumination/bromination of **4e**. Then, carbamate **9b** rearranged successfully, affording the corresponding allylamine **10b** in high yield.

The same reaction sequence was applied for the (*S*,*E*)-allyl alcohols (**8**) to afford enantiomeric (*R*)-allylamines *ent*-**10** with high overall yields (Scheme 14). The enantiopurities of allylamines **10** and *ent*-**10** were confirmed by HPLC analysis.

In the final step, allylamines **10** and *ent*-**10** were subjected to ozonolysis followed by Pinnick–Lindgren oxidation to afford the corresponding quaternary *N*-protected amino acids. To simplify their purification, these compounds were isolated as methyl esters (**13** and *ent*-**13**) obtained by treatment with trimethylsilyldiazomethane in methanol.

It should be stressed that the described method enables the direct synthesis of various *N*-functionalized allylamines with quaternary stereogenic centers. As we already demonstrated in the past,[20] the intermediate of the rearrangement step (see Scheme 7) can be easily trapped with a variety of nucleophilic

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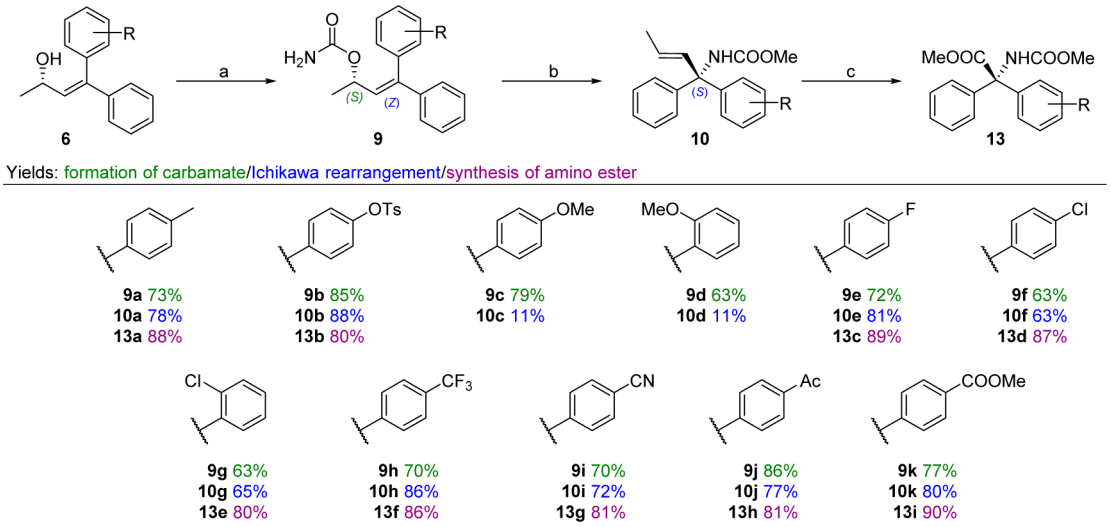
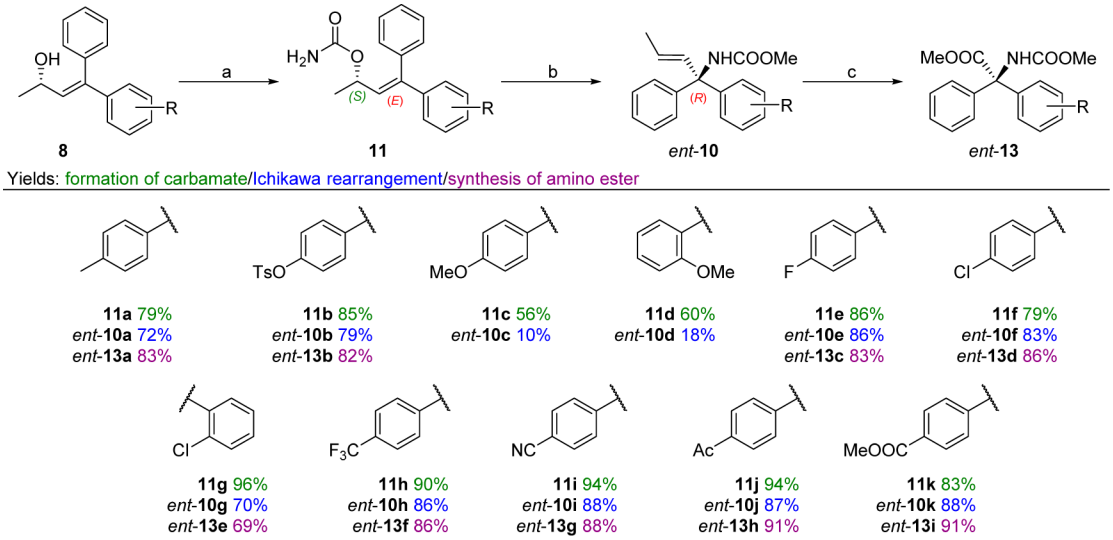
Scheme 13. Synthesis of (*S*)-Allylamines 10 and Their Conversion to Quaternary Amino Esters 13[a]



[a]Reagents and conditions: (a) i. TCAI, CH_2Cl_2; ii. aq K_2CO_3, MeOH, rt (overall, 2 steps); (b) i. TFAA, Et_3N, THF, 0 °C to rt; MeOH, Bu_3SnOMe (10 mol %), rt (overall, 3 steps); (c) i. ozonolysis, ii. Pinnick–Lindgren oxidation, iii. methylation (overall, 3 steps).

Scheme 14. Synthesis of (*R*)-Allylamines *ent*-10 and Their Conversion to Quaternary Amino Esters *ent*-13[a]



[a]Reagents and conditions: (a) i. TCAI, CH_2Cl_2; ii. aq K_2CO_3, MeOH, rt (overall, 2 steps); (b) i. TFAA, Et_3N, THF, 0 °C to rt; ii. MeOH, Bu_3SnOMe (10 mol %), rt (overall, 3 steps); (c) i. ozonolysis, ii. Pinnick–Lindgren oxidation, iii. methylation (overall, 3 steps).

reagents to provide the corresponding allyl carbamates (e.g., *N*-Boc- or *N*-Cbz-protected allylamines), amides (by treatment with Grignard of organolithium reagents), or urea derivatives (upon treatment with 1° or 2° amines, hydrazines, hydroxylamines, or ammonia). All of these functionalizations can be performed in a straightforward, one-pot manner.

■ CONCLUSIONS

In summary, we described two methods for the preparation of chiral (*E*)- and (*Z*)-*β*,*β*-diarylsubstituted allyl alcohols based on a sequential coupling strategy. The first is combination of Sonogashira and Suzuki coupling and the second involves a Sonogahira/Stille coupling sequence. As demonstrated, the second approach is more attractive because of its higher *E*/Z selectivity, which is highly important for enantioselectivity of the further described sigmatropic rearrangement step. Extended studies involving the development of protocols for the preparation of *β*-alkyl-*β*-aryl- and *β*,*β*-dialkyl-substituted allyl alcohols are currently under investigation. The obtained allyl alcohols, after their conversion into allyl carbamates, were utilized in enantiospecific synthesis of allylamines bearing a quaternary stereogenic center through the asymmetric Ichikawa rearrangement. The demonstrated method allows for the synthesis of both enantiomeric products by controlling the geometry of the double bond. As shown, the rearrangement of (*S*,*Z*)-allyl carbamates provides tertiary (*S*)-allylamines, whereas the under the same reaction conditions, (*S*,*E*)-allyl carbamates give the corresponding (*R*)-amines.

■ EXPERIMENTAL SECTION

Sonogashira Coupling of (*S*)-3-Butyn-2-ol with Aryl Iodides: General Method. Aryl iodide (1.05 equiv) was added to a mixture of (*S*)-3-butyn-2-ol (**3**) (1 equiv), CuI (0.05 equiv), and $Pd(PPh_3)_2Cl_2$ (0.01 equiv) in Et_3N (0.1 M), and the resulting mixture was kept at 60

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°C. The progress of the reaction was followed by TLC. When the reaction was complete, the reaction mixture was partitioned between brine and AcOEt. The organic layer was washed with 1 M HCl and water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel by using 5−25% AcOEt in hexanes as an eluent.

*(S)-4-(Phenyl)-but-3-yn-2-ol (**4a**).* Yield of 9.73 g (96%) starting from 5.12 g of (*S*)-3-butyn-2-ol (**3**) (97% ee); colorless oil; $[\alpha]_D^{23}$ −33.7 (*c* 1.8, $CHCl_3$) (97% ee) [lit.[24] −33.4 (*c* 1, $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.27 (m, 5H), 4.82−4.69 (m, 1H), 1.56 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.3, 128.2, 122.6, 91.0, 84.0, 58.8, 24.4; FTIR (film) ν 3339, 1598, 1490, 1443, 1330, 1106, 1038, 932, 756, 691 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{10}O$ [M] 146.0732, found 146.0732.

*(S)-4-(p-Tolyl)but-3-yn-2-ol (**4b**).* Yield of 765 mg (95%) starting from 350 mg of (*S*)-3-butyn-2-ol (**3**) (97% ee); colorless oil; $[\alpha]_D^{22}$ −31.6 (*c* 1.1, $CHCl_3$) (97% ee) [lit.[25] −27 (*c* 0.13, CH_2Cl_2)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.74 (q, *J* = 6.6 Hz, 1H), 2.34 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 131.5, 129.0, 119.5, 90.3, 84.1, 58.9, 24.4, 21.4; FTIR (film) ν 3338, 1509, 1448, 1370, 1329, 1105, 1036, 933, 817 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{11}H_{12}O$ [M] 160.0888, found 160.0890.

*(S)-4-(4-Methoxyphenyl)-but-3-yn-2-ol (**4c**).* Yield of 12.2 g (97%) starting from 5 g of (*S*)-3-butyn-2-ol (**3**) (97% ee); off-white solid; mp 44−45 °C; $[\alpha]_D^{22}$ −30.5 (*c* 1.1, $CHCl_3$) (97% ee) [lit.[26] −29.6 (*c* 1.44, $CHCl_3$)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 2H), 6.86−6.78 (m, 2H), 4.74 (qd, *J* = 6.6, 5.1 Hz, 1H), 3.79 (s, 3H), 2.20 (d, *J* = 5.1 Hz, 1H), 1.53 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 133.1, 114.7, 113.9, 89.6, 83.8, 58.8, 55.2, 24.4; HRMS (EI) *m*/*z* calcd $C_{11}H_{12}O_2$ [M] 176.0837, found 176.0832.

*(S)-4-(4-Fluorophenyl)but-3-yn-2-ol (**4d**).* Yield of 2.28 g (97%) starting from 1 g of (*S*)-3-butyn-2-ol (**3**) (97% ee); colorless oil; $[\alpha]_D^{23}$ −28.5 (*c* 1.13, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.37 (m, 2H), 7.02−6.96 (m, 2H), 4.77−4.70 (m, 1H), 1.97 (d, *J* = 6.6 Hz, 1H), 1.54 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 and 161.3 (d, J_{C-F} = 249.5 Hz), 133.6 and 133.5 (d, J_{C-F} = 8.4 Hz), 118.68 and 118.65 (d, J_{C-F} = 3.5 Hz), 115.6 and 115.4 (d, J_{C-F} = 22.1 Hz), 90.6, 82.9, 58.8, 24.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.9; FTIR (film) ν 3344, 1602, 1507, 1233, 1104, 836 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_9FO$ [M] 164.0637; found 164.0636.

*(S)-4-(3-Hydroxybut-1-yn-1-yl)phenyl 4-Methylbenzenesulfonate (**4e**).* Yield of 4.28 g (95%) starting from 1 g of (*S*)-3-butyn-2-ol (**3**) (97% ee); oil; $[\alpha]_D^{23}$ −14.8 (*c* 2.05, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.66 (m, 2H), 7.35−7.28 (m, 4H), 6.95−6.90 (m, 2H), 4.76−4.68 (m, 1H), 2.44 (s, 3H), 1.98 (d, *J* = 5.3 Hz, 1H), 1.52 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 145.5, 137.8, 133.0, 129.8, 128.5, 125.3, 122.4, 92.0, 82.7, 58.8, 24.3, 21.7; FTIR (film) ν 3534, 3365, 1598, 1498, 1375, 1199, 1176, 1155, 1093, 866, 752, 680, 563, 552 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}O_4SNa$ $[(M + Na)^+]$ 339.0667, found 339.0670.

*(S)-4-(2-Methoxyphenyl)but-3-yn-2-ol (**4f**).* Yield of 2.3 g (94%) starting from 1 g of (*S*)-3-butyne-2-ol (**3**); yellowish oil; $[\alpha]_D^{23}$ −18.2 (*c* 0.94, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.32 (m, 1H), 7.28−7.22 (m, 1H), 6.91−6.80 (m, 2H), 4.80 (p, *J* = 6.6, 5.0 Hz, 1H), 3.84 (s, 3H), 2.90 (d, *J* = 5.0 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 133.6, 129.8, 120.5, 111.8, 110.7, 95.4, 80.1, 58.8, 55.8, 24.3; HRMS (ESI-TOF) *m*/*z* calcd for $C_{11}H_{12}O_2Na$ $[(M + Na)^+]$ 199.0735, found 199.0728.

*(S)-4-(2-Chlorophenyl)but-3-yn-2-ol (**4g**).* Yield of 350 mg (97%) starting from 140 mg of (*S*)-3-butyn-2-ol (**3**) (97% ee); oil; $[\alpha]_D^{22}$ −33.3 (*c* 0.91, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.43 (m, 1H), 7.39−7.36 (m, 1H), 7.25−7.15 (m, 2H), 4.80 (q, *J* = 6.6 Hz, 1H), 2.25 (s, 1H), 1.58 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 133.4, 129.4, 129.2, 126.4, 122.5, 96.3, 80.8, 58.9, 24.3; FTIR (film) ν 3339, 1473, 1107, 1063, 1034, 754 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_9OCl$ [M] 180.0342, found 180.0348.

*(S)-4-(Naphthalen-1-yl)but-3-yn-2-ol (**4h**).* Yield of 2.57 g (91%) starting from 1 g of (S)-3-butyn-2-ol (**3**) (97% ee); $[\alpha]_D^{22}$ −30.6 (*c* 1.68, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36−8.32 (m, 1H), 7.86−7.80 (m, 2H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.60−7.55 (m, 1H), 7.52 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.40 (dd, *J* = 8.2, 7.2 Hz, 1H), 4.94 (p, *J* = 6.4 Hz, 1H), 1.68 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 133.2, 130.5, 128.9, 128.3, 126.8, 126.4, 126.1, 125.2, 120.3, 96.1, 82.1, 59.1, 24.6; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{12}ONa$ $[(M + Na)^+]$ 219.0786, found 219.0779.

*(S)-4-(Naphthalen-2-yl)but-3-yn-2-ol (**4i**).* Yield of 200 mg (97%) starting from 75 mg of (*S*)-3-butyn-2-ol (**3**) (97% ee); $[\alpha]_D^{19}$ −32.6 (*c* 0.8, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.84−7.74 (m, 3H), 7.53−7.45 (m, 3H), 4.81 (qd, *J* = 6.6, 5.3 Hz, 1H), 1.94 (d, *J* = 5.3 Hz, 1H), 1.60 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 132.9, 131.6, 128.4, 128.0, 127.7, 126.7, 126.5, 119.9, 91.2, 84.4, 59.0, 24.5; HRMS (ESI-TOF) *m*/*z* calcd for $C_{14}H_{12}ONa$ $[(M + Na)^+]$ 219.0786, found 219.0783.

Hydroalumination/Halogenation of Alkynes 5: General Method. A 3.6 M solution of Red-Al (22 mmol) was added over 10 min to a solution of alkyne (10 mmol) in 50 mL of dry THF (0.2M) and cooled to −30 °C. The reaction mixture was heated to 0 °C. The progress of the reduction was followed by TLC. When the reduction was complete, the reaction mixture was cooled to −78 °C, and a solution of I_2 or Br_2 (21 mmol) in 34 mL of dry THF was added slowly. The progress of the reaction was followed by TLC. When the halogenation was complete, the reaction was quenched by the addition of sat. aq $Na_2S_2O_3$. After stirring for 5 min, the mixture was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel.

*(S,Z)-4-Iodo-4-phenylbut-3-en-2-ol (**5a**).* Yield of 2.6 g (90%) starting from 1.46 g of alkyne **4a**; colorless oil; $[\alpha]_D^{24}$ −14.5 (c 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (m, 2H), 7.34−7.26 (m, 3H), 6.00 (d, *J* = 7.3 Hz, 1H), 4.69−4.60 (m, 1H), 1.39 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 141.4, 128.7, 128.5, 128.3, 104.2, 73.5, 21.9; FTIR (film) ν 3341, 1488, 1442, 1138, 1061, 884, 757, 693, 618 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{11}IO$ [M] 273.9855, found 273.9844.

*(S,Z)-4-Bromo-4-phenylbut-3-en-2-ol (**5b**).* Yield of 2.1 g (92%) starting from 1.46 g of alkyne **4a**; *Z*/*E* ratio of 15:1 (NMR); $[\alpha]_D^{23}$ −19.4 (*c* 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59−7.27 (m, 5H), 6.29 (d, *J* = 7.4 Hz, 1H), 4.95−4.78 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 134.7, 128.9, 128.3, 127.6, 125.2, 68.7, 22.1; FTIR (film) ν 3340, 1632, 1490, 1444, 1063, 890, 758, 692, 636 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{10}H_{11}OBr$ [M] 225.9993, found 225.9998.

*(S,Z)-4-Bromo-4-(p-tolyl)but-3-en-2-ol (**5c**).* Yield of 930 mg (85%) starting from 730 mg of alkyne **4b**; brown oil; *Z*/*E* ratio of 10:1 (NMR); $[\alpha]_D^{21.5}$ −19.0 (*c* 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 7.4 Hz, 1H), 4.90−4.79 (m, 1H), 2.36 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.3, 133.9, 129.0, 127.5, 125.4, 68.7, 22.1, 21.1; FTIR (film) ν 3335, 1509, 1063, 812, 611 cm^{-1}; HRMS (EI) *m*/*z* calcd $C_{11}H_{13}OBr$ [M] 240.0150, found 240.0150.

*(S,Z)-4-Bromo-4-(4-fluorophenyl)but-3-en-2-ol (**5d**).* Yield of 200 mg (82%) starting from 164 mg of alkyne **4d**; brown oil; *Z*/*E* ratio of 15:1 (NMR); $[\alpha]_D^{23}$ −18.3 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 2H), 7.04−6.98 (m, 2H), 6.22 (d, *J* = 7.4 Hz, 1H), 4.82 (dq, *J* = 7.4, 6.4 Hz, 1H), 2.36 (s, 1H), 1.38 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 and 161.7 (d, J_{C-F} = 249.4 Hz), 135.27 and 135.24 (d, J_{C-F} = 3.3 Hz), 134.84, 134.82, 129.4, and 129.3 (d, J_{C-F} = 8.4 Hz), 123.8, 115.3 and 115.1 (d, J_{C-F} = 22.0), 68.7, 22.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −112.4; HRMS (EI) *m*/*z* calcd for $C_{10}H_{10}OFBr$ [M] 243.9899, found 243.9908.

*(S,Z)-4-(1-Bromo-3-hydroxybut-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**5f**).* Yield of 169 mg (92%) starting from 142 mg of alkyne **4e**; brown oil; *Z*/*E* ratio of 35:1 (NMR); $[\alpha]_D^{23}$ −12.9 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.48−7.42 (m, 2H), 7.33−7.29 (m, 2H), 6.97−6.92 (m, 2H), 6.25 (d, *J* = 7.3 Hz, 1H), 4.80 (dq, *J* = 7.3, 6.4 Hz, 1H), 2.44 (s, 3H), 1.36 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 145.6, 135.78,

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135.77, 132.3, 129.9, 128.8, 128.5, 122.23, 122.20, 68.7, 22.1, 21.7; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}O_4SBrNa$ [(M + Na)$^+$] 418.9929, found 418.9919.

Synthesis of β,β-Disubstituted Allyl Alcohols via Suzuki Coupling: General Method. A solution of vinyl bromide **5** (1 mmol) in 4 mL of degassed toluene was added to a solution of arylboronic acid (1.3 mmol), Cs_2CO_3 (3 mmol), and $Pd(PPh_3)_4$ (0.05 mmol). Next, 0.5 mL of degassed water was added, and the reaction mixture was stirred under argon at 60 °C for 18−24 h. The progress of the reaction was followed by TLC or NMR. Next, the solvent was removed under reduced pressure, and the residue was chromatographed on silica gel using 0−15% AcOEt in hexanes as the eluent.

(S,Z)-4-Phenyl-4-(p-tolyl)but-3-en-2-ol ***(6a)***. Yield of 170 mg (71%) starting from 227 mg of vinyl bromide **5b**; *Z*:*E* ratio of 13:1; analytic sample obtained by preparative TLC (SiO_2, 15% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ −45.1 (*c* 1.3, $CHCl_3$, 94% ee, HPLC R_t = 8.17 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 5H), 7.20−7.17 (m, 2H), 7.10−7.06 (m, 2H), 6.05 (d, *J* = 9.0 Hz, 1H), 4.45−4.36 (m, 1H), 2.39 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 141.2, 137.1, 132.2, 129.6, 128.9, 128.1, 127.5, 65.8, 23.7, 21.2; FTIR (film) ν 3341, 1512, 1444, 1053, 823, 765, 698, 633 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}ONa$ [(M + Na)$^+$] 261.1255, found 261.1255; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 8.16 min (*S*-isomer) and 10.53 min (*R*-isomer).

(S,Z)-4-(Naphthalen-2-yl)-4-phenylbut-3-en-2-ol ***(6b)***. Yield of 140 mg (51%) starting from 227 mg of vinyl bromide **5b**; brown oil; analytic sample obtained by preparative TLC (SiO_2, 5% AcOEt in hexanes); $[\alpha]_D^{29}$ −40.6 (*c* 0.94, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.80 (m, 3H), 7.75−7.69 (m, 1H), 7.55−7.48 (m, 2H), 7.32−7.23 (m, 6H), 6.18 (d, *J* = 9.1 Hz, 1H), 4.46 (dq, *J* = 9.1, 6.2 Hz, 1H), 1.37 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.6, 136.8, 133.2, 132.7, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.6, 126.4, 126.3, 126.1, 65.8, 23.8; FTIR (film) ν 3353, 1598, 1493, 1445, 1137, 1054, 818, 762, 749, 698, 479 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{18}ONa$ [(M + Na)$^+$] 297.1255, found 297.1255.

(S,Z)-4-(Naphthalen-1-yl)-4-phenylbut-3-en-2-ol ***(6c)***. Not isolated in a pure form; yield of 110 mg (41%, assigned by ^{1}H NMR of crude reaction mixture with internal standard) starting from 220 mg of vinyl bromide **5b**; ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers, selected signals) δ 6.45 (d, *J* = 8.9 Hz, 1H), 6.44 (d, *J* = 9.0 Hz, 1H), 4.14−4.03 (m, 2H), 1.55 (s, 2H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). HRMS (ESI-TOF) m/z calcd for $C_{20}H_{18}ONa$ [(M + Na)$^+$] 297.1255, found 297.1255.

(S,Z)-4-(4-Methoxyphenyl)-4-phenylbut-3-en-2-ol ***(6d)***. Yield of 170 mg (67%) starting from 227 mg of vinyl bromide **5b**; *Z*/*E* ratio of 14:1; analytic sample obtained by preparative TLC (SiO_2, 15% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ −48.6 (*c* 1.12, $CHCl_3$) (89% ee, HPLC, R_t = 11.41 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.22 (m, 5H), 7.14−7.09 (m, 2H), 6.94−6.88 (m, 2H), 6.02 (d, *J* = 9.0 Hz, 1H), 4.43 (dq, *J* = 9.0, 6.3 Hz, 1H), 3.84 (s, 3H), 1.61 (s, 1H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 142.3, 142.1, 132.1, 131.6, 130.9, 128.1, 127.6, 127.5, 113.6, 65.8, 55.2, 23.7; FTIR (film) ν 3353, 1607, 1511, 1245, 1034, 766 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 277.1204, found 277.1199; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 11.34 min (*S*-isomer) and 16.48 min (*R*-isomer).

(S,Z)-4-(2-Methoxyphenyl)-4-phenylbut-3-en-2-ol ***(6e)***. Yield of 173 mg (68%) starting from 227 mg of vinyl bromide **5b** after 30 h; colorless oil; $[\alpha]_D^{22}$ −5.6 (*c* 1.3, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−6.98 (m, 9H), 6.21 (d, *J* = 9.1 Hz, 1H), 4.20 (dq, *J* = 9.1, 6.2 Hz, 1H), 3.75 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 141.0, 138.3, 133.1, 131.3, 129.0, 128.6, 128.2, 127.4, 126.7, 121.0, 111.4, 66.1, 55.8, 22.6; FTIR (film) ν 3377, 1598, 1490, 1245, 1048, 1027, 755, 695 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 277.1204, found 277.1203.

(S,Z)-4-(4-Fluorophenyl)-4-phenylbut-3-en-2-ol ***(6f)***. Yield of 390 mg (77%) starting from 476 mg of vinyl bromide **5b**; *Z*/*E* ratio of 27:1 (NMR); colorless oil; $[\alpha]_D^{22}$ −43.8 (*c* 1.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.02 (m, 9H), 6.07 (d, *J* = 9.1 Hz, 1H), 4.41−4.29 (m, 1H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4 and 160.9 (d, J_{C-F} = 246.8 Hz), 141.64, 141.58, 135.20 and 135.17 (d, J_{C-F} = 3.6 Hz), 132.6, 131.4 and 131.3 (d, J_{C-F} = 7.9 Hz), 128.2, 127.7, 127.4, 115.4 and 115.1 (d, J_{C-F} = 21.4 Hz), 65.7, 23.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.6; FTIR (film) ν 3340, 1602, 1508, 1223, 1054, 839, 766, 697 cm^{-1}; HRMS (EI) m/z calcd for $C_{16}H_{15}OF$ [M] 242.1107, found 242.1113.

(S,Z)-4-(4-Chlorophenyl)-4-phenylbut-3-en-2-ol ***(6g)***. Yield of 230 mg (89%) starting from 227 mg of vinyl bromide **5b**; colorless oil; *Z*/*E* ratio of 16:1 (NMR); $[\alpha]_D^{22}$ −41.2 (*c* 1, $CHCl_3$) (94% ee (*Z*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 2H), 7.29−7.25 (m, 3H), 7.23−7.20 (m, 2H), 7.16−7.12 (m, 2H), 6.08 (d, *J* = 9.1 Hz, 1H), 4.36 (dq, *J* = 9.1, 6.3 Hz, 1H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 141.3, 137.7, 132.8, 131.1, 128.5, 128.3, 127.8, 127.4, 126.4, 65.7, 23.8; FTIR (film) ν 3338, 1491, 1090, 1055, 829, 758, 696 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{14}Cl$ [(M − OH)$^+$] 241.0784, found 241.0782.

(S,Z)-4-(2-Chlorophenyl)-4-phenylbut-3-en-2-ol ***(6h)***. Yield of 156 mg (60%) starting from 227 mg of vinyl bromide **5b** after 30 h; colorless oil; $[\alpha]_D^{22}$ −26.1 (*c* 1, $CHCl_3$); ^{1}H NMR (600 MHz, PhMe-d_7, 80 °C) δ 7.20−7.15 (m, 2H), 7.08−6.83 (m, 7H), 6.12 (d, *J* = 8.8 Hz, 1H), 4.07 (p, *J* = 8.8, 6.2 Hz, 1H), 1.15 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (151 MHz, PhMe-d_7, 80 °C) δ 139.9, 138.5, 134.1, 131.3, 129.5, 128.6, 128.4, 128.0, 127.7, 127.2, 126.4, 126.3, 65.7, 22.7; FTIR (film) ν 3357, 1494, 1472, 1445, 1433, 1367, 1141, 1050, 947, 761, 750, 694, 632, 597 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{15}OClNa$ [(M + Na)$^+$] 281.0709, found 281.0696

(S,Z)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-2-ol ***(6i)***. Yield of 269 mg (92%) starting from 227 mg of vinyl bromide **5b**; yellowish oil; $[\alpha]_D^{29}$ −23.8 (*c* 1.09, $CHCl_3$) (97.5%ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.41−7.18 (m, 7H), 6.13 (d, *J* = 9.2 Hz, 1H), 4.38−4.25 (m, 1H), 1.34 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 141.0, 138.8, 134.1 129.97, 129.66, 129.33 and 129.01 (q, J_{C-F} = 32.6 Hz), 129.58, 128.49, 127.81, 127.68, 128.31, 125.52, 122.81 and 120.11 (q, J_{C-F} = 272.0 Hz), 125.17, 125.13, 125.11 and 125.05 (q, J_{C-F} = 3.7 Hz), 65.2, 23.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6; FTIR (film) ν 3343, 1325, 1166, 1126, 1108, 1066, 840, 766, 969, 640 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{14}F_3$ [(M − OH)$^+$] 275.1048, found 275.1043.

(S,Z)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)benzonitrile ***(6j)***. Yield of 153 mg (61%) starting from 227 mg of vinyl bromide **5b**; colorless oil; $[\alpha]_D^{21}$ −8.8 (*c* 1.36, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.19−7.15 (m, 2H), 6.13 (d, *J* = 9.3 Hz, 1H), 4.28 (dq, *J* = 9.3, 6.3 Hz, 1H), 1.86 (s, 1H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 141.0, 140.6, 133.7, 132.1, 130.5, 128.4, 128.1, 127.4, 118.7, 111.4, 65.5, 23.9; FTIR (film) ν 3408, 1604, 1445, 1370, 1133, 1055, 838, 765, 698, 633, 554 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{15}NONa$ [(M + Na)$^+$] 272.1051, found 272.1050

(S,Z)-1-(4-(3-Hydroxy-1-phenylbut-1-en-1-yl)phenyl)ethan-1-one ***(6k)***. Yield of 243 mg (91%) starting from 227 mg of vinyl bromide **5b**; *Z*/*E* ratio of 16:1; analytic sample obtained by preparative TLC (SiO_2, 20% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23}$ −15.5 (*c* 1.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.33−7.18 (m, 7H), 6.13 (d, *J* = 9.2 Hz, 1H), 4.34 (dq, *J* = 9.2, 6.2 Hz, 1H), 2.63 (s, 3H), 1.35 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 144.5, 141.7, 141.0, 136.2, 133.1, 130.9, 130.0, 128.4, 128.3, 127.9, 127.4, 65.7, 26.6, 23.8; FTIR (film) ν 3397, 1682, 1604, 1359, 1269, 1055, 764, 698, 635 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}O_2Na$ [(M + Na)$^+$] 289.1204, found 289.1203.

Methyl (S,Z)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)benzoate ***(6l)***. Yield of 200 mg (71%) starting from 227 mg of vinyl bromide **5b**; colorless oil; *Z*/*E* ratio of 20:1; analytic sample obtained by preparative TLC (SiO_2, 20% AcOEt in hexanes); $[\alpha]_D^{22}$ −31.2 (*c* 1.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.34−7.16 (m, 7H), 6.12 (d, *J* = 9.2 Hz, 1H), 4.34 (dq, *J* = 9.1, 6.2 Hz, 1H), 3.93 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 144.3, 141.7, 141.0, 133.0, 129.8, 129.6, 129.3, 128.3, 127.8, 127.4, 65.7, 52.2, 23.7; FTIR (film) ν 3418, 1722, 1607, 1437, 1281,

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1114, 1103, 1055, 765, 712, 698 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}O_3Na$ $[(M + Na)^+]$ 305.1154, found 305.1143.

*(S,E)-4-Phenyl-4-(p-tolyl)but-3-en-2-ol (**8a**).* Yield of 209 mg (88%) starting from 241 mg of vinyl bromide **5c**; Z/E ratio of 12:1; analytic sample obtained by preparative TLC (SiO_2, 15% AcOEt in hexanes); colorless oil; $[\alpha]_D^{23.5}$ −48.4 (c 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.05 (m, 9H), 6.05 (d, J = 9.1 Hz, 1H), 4.38 (dq, J = 9.1, 6.3 Hz, 1H), 2.33 (s, 3H), 1.33 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 138.9, 137.4, 131.5, 129.6, 128.9, 128.2, 127.3, 65.8, 23.7, 21.1; FTIR (film) ν 3340, 1511, 1442, 1368, 1053, 818, 702, 599 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}ONa$ $[(M + Na)^+]$ 261.1255, found 261.1251; HPLC (rac) Chiralpak IB, 10% i-PrOH in hexanes, 1 mL/min, R_t = 8.25 min (S-isomer) and 9.47 min (R-isomer).

*(S,E)-4-Phenyl-3-butene-2-ol (**7**).* Debromination side product; $[\alpha]_D^{23}$ −31.2 (c 1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.21 (m, 5H), 6.57 (br d, J = 15.9 Hz, 1H), 6.27 (dd, J = 15.9, 6.4 Hz, 1H), 4.50 (pd, J = 6.4, 1.2 Hz, 1H), 1.38 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 133.6, 129.4, 128.6, 127.6, 126.4, 68.9, 23.4; IR (film) ν 3429, 3394 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{10}H_{12}ONa$ $[(M + Na)^+]$ 171.0786, found 171.0784.

Hydrostannylation of Propargyl Alcohols 12: General Method. A solution of propargyl alcohol (1 mmol) in 1 mL of THF was added to $Pd(PPh_3)_2Cl_2$ (0.01 mmol) in 1 mL of THF under argon. After 15 min, the solution was cooled to −5 °C, and Bu_3SnH (1.1 mmol) was added slowly; the resulting mixture was heated to rt. The progress of the reaction was followed by TLC. When the reaction was complete, sat. aq NH_4Cl was added, and the resulting mixture was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4, and the solvent was removed. The residue was purified by flash column chromatography on silica gel.

*(S,E)-4-Phenyl-4-(tributylstannyl)but-3-en-2-ol (**12a**).* Yield of 2 g (92%) starting from 702 mg of alkyne **4a**; colorless oil; $[\alpha]_D^{22}$ −25.8 (c 1.3, $CHCl_3$), 97.3% ee, R_t = 11.68 min for 4-nitrobenzoate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.24 (m, 2H), 7.12 (tt, J = 6.9, 1.2 Hz, 1H), 6.94−6.89 (m, 2H), 5.79 (d, J = 8.3 Hz, 1H), 4.36 (p, J = 8.3, 6.3 Hz, 1H), 1.49−1.23 (m, 18H), 1.22 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 144.7, 144.3, 128.1, 126.4, 125.1, 65.1, 28.9, 27.2, 23.6, 13.6, 9.9; FTIR (film) ν 3336, 1461, 1053, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{38}OSnNa$ $[(M + Na)^+]$ 461.1842, found 461.1843; HPLC (for 4-nitrobenzoate, rac) Chiralpak IB, 1% i-PrOH in hexanes, 0.5 mL/min, R_t = 11.9 min (S-isomer) and 13.2 min (R-isomer).

*(S,E)-4-(p-Tolyl)-4-(tributylstannyl)but-3-en-2-ol (**12b**).* Yield of 702 mg (93%) starting from 270 mg of alkyne **4b**; colorless oil; $[\alpha]_D^{22}$ −25.6 (c 1.44, $CHCl_3$, 97% ee HPLC); ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 2H), 5.77 (d, J = 8.3 Hz, 1H), 4.42−4.33 (m, 1H), 1.56−1.21 (m, 18H), 1.22 (d, J = 6.3 Hz), 0.92−0.82 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 144.7, 141.2, 134.6, 128.8, 126.4, 65.1, 28.9, 27.3, 23.6, 13.6, 9.9; FTIR (film) ν 3327, 1505, 1463, 1376, 1053 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{40}SnONa$ $[(M + Na)^+]$ 475.1999, found 475.2007; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, 0.5 mL/min, R_t = 14.25 in and 14.73 min.

*(S,E)-4-(Naphthalen-2-yl)-4-(tributylstannyl)but-3-en-2-ol (**12c**).* Yield of 225 mg (92%) starting from 98.1 mg of alkyne **4i**; $[\alpha]_D^{20.5}$ −20.5 (c 1.01, $CHCl_3$) (98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83−7.73 (m, 3H), 7.48−7.38 (m, 2H), 7.37−7.33 (m, 1H), 7.10 (dd, J = 8.4, 1.8 Hz, 1H), 5.88 (d, J = 8.3 Hz, 1H), 4.40 (p, J = 6.5 Hz, 1H), 1.51−1.42 (m, 6H), 1.32−1.22 (m, 9H), 0.96−0.89 (m, 6H), 0.85 (t, J = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 145.1, 142.1, 133.5, 131.5, 127.8, 127.7, 127.5, 126.1, 125.9, 125.1, 124.0, 65.3, 29.0, 27.3, 23.6, 13.6, 10.0; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{40}OSnNa$ $[(M + Na)^+]$ 511.1999, found 511.1997.

*(S,E)-4-(Naphthalen-1-yl)-4-(tributylstannyl)but-3-en-2-ol (**12d**).* Yield of 480 mg (98%) starting from 196 mg of alkyne **4h**; colorless oil; $[\alpha]_D^{23}$ −1 (c 1.42, $CHCl_3$); ^1H NMR (600 MHz, toluene-d_7, 80 °C, mixture of rotamers 1:1) δ 8.07 (d, J = 8.3 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.64−6.94 (m, 12H), 6.17 (d, J = 7.9 Hz, 0H), 6.15 (d, J = 8.0 Hz, 0H), 4.15−4.08 (m, 1H), 4.08−4.01 (m, 1H), 1.50−1.39 (m, 12H), 1.27−1.19 (m, 12H), 1.09 (d, J = 6.3 Hz, 3H), 1.01 (d, J = 6.3 Hz, 3H), 0.95−0.79 (m, 30H); ^{13}C NMR (151 MHz, toluene-d_7, 80 °C, mixture of rotamers 1:1) δ 147.4, 147.2, 144.8, 143.7, 142.3, 142.1, 134.1, 134.0, 130.7, 130.1, 128.6, 127.7, 125.59, 125.56, 125.5, 125.3, 125.0, 124.9, 123.0, 122.4, 65.7, 65.3, 28.8, 27.0, 23.5, 22.8, 13.1, 10.4, 10.3; FTIR (film) ν 3343, 1463, 1392, 1055, 783 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{40}OSnNa$ $[(M + Na)^+]$ 511.1999, found 511.2002.

*(S,E)-4-(4-Methoxyphenyl)-4-(tributylstannyl)but-3-en-2-ol (**12e**).* Yield of 4.0 g (97%) starting from 1.6 g of alkyne **4c**; colorless oil; $[\alpha]_D^{23}$ −30.5 (c 1.53, $CHCl_3$) (98.4% ee, R_t = 22.3 min); ^1H NMR (400 MHz, $CDCl_3$) δ 6.89−6.79 (m, 4H), 5.77 (d, J 8.3 Hz, 1H), 4.45−4.34 (m, 1H), 3.79 (s, 3H), 1.52−1.24 (m, 18H), 1.23 (d, J 6.3 Hz, 3H), 0.94−0.81 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 146.5, 145.0, 136.6, 127.6, 113.6, 65.0, 28.9, 27.3, 23.6, 9.9; FTIR (film) ν 3343, 1601, 1504, 1464, 1281, 1243, 1038, 662 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{40}O_2SnNa$ $[(M + Na)^+]$ 491.1948, found 491.1956; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, 0.5 mL/min, R_t = 21.66 min (R-isomer) and 22.33 min (S-isomer).

*(S,E)-4-(3-Hydroxy-1-(tributylstannyl)but-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**12f**).* Yield of 570 mg (94%) starting from 316 mg of alkyne **4e**; yellowish oil; $[\alpha]_D^{21}$ −16.5 (c 1.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.90−6.86 (m, 2H), 6.83−6.79 (m, 2H), 5.77 (d, J = 8.4 Hz, 1H), 4.30−4.20 (m, 1H), 2.43 (s, 3H), 1.47−1.17 (m, 18H), 1.19 (d, J = 6.3 H, 3H), 0.88−0.82 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 145.7, 145.4, 145.2, 143.4, 132.5, 129.6, 128.5, 127.5, 122.2, 65.1, 28.9, 27.2, 23.6, 21.7, 13.6, 10.0; FTIR (film) ν 3554, 1494, 1376, 1198, 1176, 1152, 1094, 864, 813, 553 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{44}O_4SSnNa$ $[(M + Na)^+]$ 631.1880, found 631.1886.

*(S,E)-4-(2-Methoxyphenyl)-4-(tributylstannyl)but-3-en-2-ol (**12g**).* Yield of 431 mg (92%) starting from 176 mg of alkyne **4f**; colorless oil; $[\alpha]_D^{22}$ +7.94 (c 1.46, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16−7.10 (m, 1H), 6.92−6.80 (m, 3H), 5.81 (d, J = 8.4 Hz, 1H), 4.27 (dq, J = 8.4, 6.3 Hz, 1H), 3.76 (s, 3H), 1.86 (s, 1H), 1.47−1.38 (m, 6H), 1.30−1.22 (m, 6H), 1.21 (d, J = 6.3 Hz, 3H), 0.93−0.71 (m, 15H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6, 144.9, 143.4, 128.0, 126.7, 120.5, 110.2, 65.3, 55.1, 28.9, 22.7, 13.7, 10.2; FTIR (film) ν 3397, 1484, 1462, 1239, 1108, 1048, 1029, 749 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{40}O_2SnNa$ $[(M + Na)^+]$ 491.1948, found 491.1994.

*(S,E)-4-(2-Chlorophenyl)-4-(tributylstannyl)but-3-en-2-ol (**12h**).* Yield of 840 mg (96%) starting from 334 mg of alkyne **4g**; colorless oil; $[\alpha]_D^{23}$ +7.0 (c 0.94, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.29 (m, 1H), 7.22−7.13 (m, 1H), 7.11−7.05 (m, 1H), 7.00−6.83 (m, 1H), 5.85 (d, J = 8.3 Hz, 1H), 4.25−4.06 (m, 1H), 1.48−1.38 (m, 6H), 1.30−1.21 (m, 6H), 1.19 (d, J = 6.3 Hz, 4H), 0.93−0.87 (m, 6H), 0.85 (t, J = 7.3 Hz, 9H); ^{13}C NMR (151 MHz, PhMe-d_7) δ 146.8, 143.2, 129.1, 128.6, 127.7, 126.3(×2), 126.2, 65.5, 28.8, 27.0, 22.7, 13.1, 10.6; FTIR (film) ν 3341, 1463, 1048, 742 cm^{-1}; HRMS (ESI-TOF) m/z $C_{22}H_{37}ClOSnNa$ $[(M + Na)^+]$ 495.1453, found 495.1437.

*(S,E)-4-(4-Fluorophenyl)-4-(tributylstannyl)but-3-en-2-ol (**12i**).* Yield of 462 mg (81%) starting from 205 mg of alkyne **4d**; colorless oil; $[\alpha]_D^{22}$ −22.4 (c 1.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.00−6.94 (m, 2H), 6.90−6.85 (m, 2H), 5.80 (d, J = 8.3 Hz, 1H), 4.39−4.28 (m, 1H), 1.50−1.20 (m, 18H), 1.22 (d, J = 6.3 H, 3H), 0.91−0.83 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 and 159.6 (d, J_{C-F} 243.8 Hz), 146.0, 145.4, 145.4, 140.2 and 140.1 (d, J_{C-F} = 3.3 Hz), 127.9 and 127.8 (d, J_{C-F} = 7.9 Hz), 115.1 and 114.9 (d, J_{C-F} = 21.3 Hz), 65.0, 28.9, 27.2, 23.6, 13.6, 9.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.2; FTIR (film) ν 3331, 1596, 1501, 1222, 1053 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{37}OSnFNa$ $[(M + Na)^+]$ 479.1748, found 479.1751.

Synthesis of β,β-Disubstituted Allyl Alcohols via Stille Coupling: Genaral Method. $Pd(PPh_3)_4$ (5 mol %, 0.05 mmol, 58 mg), CuI (10 mol %, 0.1 mmol, 19 mg), and CsF (2 mmol, 300 mg) were added to a solution of vinyltributylstannane (1 mmol) and aryl iodide (1.3 mmol) in 2.2 mL of degassed THF. The resulting mixture was kept at 45 °C for 18−20 h. Next, the solvent was removed. The

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residue was supported on silica gel and chromatographed on silica gel (0−20% AcOEt in hexanes).

*(S,E)-4-Phenyl-4-(p-tolyl)but-3-en-2-ol (**8a**).* Yield of 220 mg (92%) starting from vinyl stannane **12a**; $[\alpha]_D^{23.5}$ −50.3 (*c* 0.75, $CHCl_3$) (97% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44−7.05 (m, 9H), 6.05 (d, *J* = 9.1 Hz, 1H), 4.38 (dq, *J* = 9.1, 6.3 Hz, 1H), 2.33 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}ONa$ [(M + Na)$^+$] 261.1255, found 261.1251; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 8.25 min (*S*-isomer) and 9.47 min (*R*-isomer).

*(S,E)-4-(Naphthalen-1-yl)-4-phenylbut-3-en-2-ol (**8b**).* Yield of 140 mg (45%) starting from 437 mg of vinyl stannane **12a** (54% conversion after 3 days); colorless oil; $[\alpha]_D^{22}$ −8.0 (*c* 0.97, $CHCl_3$) (97.2% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.92 (m, 1H), 7.86−7.78 (m, 2H), 7.49−7.23 (m, 9H), 5.91 (d, *J* = 9.3 Hz, 1H), 4.84−4.74 (m, 1H), 1.47 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.9, 140.1, 136.2, 133.9, 131.7, 129.0, 128.3, 128.2, 127.9, 127.5, 127.2, 126.0 (×2), 125.6, 125.2, 65.3, 24.1; FTIR (film) ν 3341, 1053, 882, 774, 701 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{18}ONa$ [(M + Na)$^+$] 297.1255, found 297.1254; HPLC Chiralpak IB, 1% *i*-PrOH in hexanes, 1 mL/min, R_t = 30.83 min (*R*-isomer) and 36.63 min (*S*-isomer).

*(S,E)-4-(4-Methoxyphenyl)-4-phenylbut-3-en-2-ol (**8c**).* Yield of 175 mg (69%) starting from 437 mg of vinyl stannane **12a**; yellow oil; $[\alpha]_D^{22}$ −62.9 (*c* 1.49, $CHCl_3$) (97% ee, HPLC R_t = 10.1 min); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.31 (m, 3H), 7.19 (ddd, *J* = 9.3, 5.2, 2.4 Hz, 4H), 6.88−6.78 (m, 2H), 6.02 (d, *J* = 9.1 Hz, 1H), 4.37 (dq, *J* = 9.1, 6.3 Hz, 1H), 3.79 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 141.9, 139.6, 134.4, 130.8, 129.7, 128.6, 128.2, 127.4, 113.6, 65.7, 55.3, 23.8; FTIR (film) ν 3363, 1605, 1510, 1249, 1181, 1035, 830, 702 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 277.1204, found 277.1200; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 10.29 min (*S*-isomer) and 12.43 min (*R*-isomer).

*(S,E)-4-(2-Methoxyphenyl)-4-phenylbut-3-en-2-ol (**8d**).* Yield of 85 mg (67%) starting from 218 mg of vinylstannane **12a** (66% conversion after 48 h); $[\alpha]_D^{21}$ −43.2 (*c* 0.51, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32−7.16 (m, 7H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.84 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.88 (d, *J* = 9.2 Hz, 1H), 4.53 (dq, *J* = 9.2, 6.2 Hz, 1H), 3.58 (s, 3H), 1.72 (s, 1H), 1.36 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 140.5, 140.3, 134.9, 132.4, 130.8, 128.9, 128.8, 127.8, 126.9, 120.5, 111.7, 65.3, 55.6, 23.7; FTIR (film) ν 3367, 1597, 1489, 1249, 1051, 1027, 753, 701 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 277.1204, found 277.1200.

*(S,E)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**8e**).* Yield of 440 mg (97%) starting from 503 mg of vinyl stannane **12a**; colorless oil; $[\alpha]_D^{23}$ −34.5 (*c* 0.22, $CHCl_3$) (96% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.39−7.28 (m, 5H), 7.17−7.11 (m, 4H), 6.90−6.85 (m, 2H), 6.03 (d, *J* = 9.0 Hz, 1H), 4.34 (dq, *J* = 9.0, 6.2 Hz, 1H), 2.44 (s, 3H), 1.61 (s, 1H), 1.30 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 145.4, 141.2, 140.6, 138.8, 133.2 (x2), 132.5, 129.8, 129.6, 128.5, 128.4, 127.7, 122.0, 65.7, 23.7, 21.7; FTIR (film) ν 3552, 3379, 1597, 1499, 1377, 1199, 1178, 1154, 1093, 866, 843, 712, 566 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{22}O_4SNa$ [(M + Na)$^+$] 417.1136, found 417.1132.

*(S,E)-4-(4-Fluorophenyl)-4-phenylbut-3-en-2-ol (**8f**).* Yield of 195 mg (80%) starting from 437 mg of vinyl stannane **12a**; colorless oil; $[\alpha]_D^{23}$ −47.7 (*c* 0.95, $CHCl_3$) (98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.16 (m, 9H), 6.99−6.93 (m, 2H), 6.02 (d, *J* = 9.1 Hz, 1H), 4.37 (dq, *J* = 9.1, 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6 and 161.2 (d, J_{C-F} = 247.1 Hz), 141.5, 139.2, 137.88 and 137.86 (d, J_{C-F} = 3.2 Hz), 132.3, 129.6, 129.1 and 129.0 (d, J_{C-F} = 8.0 Hz), 128.4, 127.6, 115.1 and 114.9 (d, J_{C-F} = 21.4 Hz), 65.7, 23.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.9; FTIR (film) ν 3340, 1602, 1508, 1230, 1159, 1054, 834, 702, 597, 569 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{16}H_{15}OF$ [M] 242.1107, found 242.1112.

*(S,E)-4-(4-Chlorophenyl)-4-phenylbut-3-en-2-ol (**8g**).* Yield of 75 mg (85%) starting from 148 mg of vinyl stannane **12a**; colorless oil; $[\alpha]_D^{22}$ −45.7 (*c* 0.54, $CHCl_3$) (96.6% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42−7.13 (m, 9H), 6.06 (d, *J* = 9.0 Hz, 1H), 4.38 (dq, *J* = 9.1, 6.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 140.2, 138.9, 133.5, 132.7, 129.6, 128.7, 128.4, 128.3, 127.7, 65.7, 23.7; FTIR (film) ν 3340, 1490, 1442, 1402, 1368, 1091, 1055, 827, 775, 744, 704, 593, 505 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{16}H_{15}OCl$ [M] 258.0811, found 258.0813.

*(S,E)-4-(2-Chlorophenyl)-4-phenylbut-3-en-2-ol (**8h**).* Yield of 130 mg (84%) starting from 262 mg of vinyl stannane **12a**; solid/oil; $[\alpha]_D^{21}$ −23.4 (*c* 0.74, $CHCl_3$) (97% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.17 (m, 9H), 5.78 (d, *J* = 9.2 Hz, 1H), 4.63 (dq, *J* = 9.2, 6.3 Hz, 1H), 1.64 (s, 1H), 1.40 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.5, 138.8, 136.3, 133.2, 131.4, 129.9, 129.2, 128.6, 128.0, 127.5, 126.5, 65.2, 23.7; HRMS (EI) *m*/*z* calcd $C_{16}H_{15}ClO$ [M] 258.0811, found 258.0813.

*(S,E)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-2-ol (**8i**).* Yield of 280 mg (96%) starting from 437 mg of vinyl stannane **12a**; colorless oil; $[\alpha]_D^{21}$ −36.3 (*c* 0.75, $CHCl_3$) (97.4% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.51 (m, 2H), 7.43−7.37 (m, 3H), 7.36−7.33 (m, 2H), 7.20−7.16 (m, 2H), 6.14 (d, *J* = 9.0 Hz, 1H), 4.46−4.37 (m, 1H), 1.68 (s, 1H), 1.35 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 141.3, 138.5, 134.3, 129.98, 129.66, 129.33 and 129.01 (q, J_{C-F} = 32.6 Hz), 129.58, 128.49, 127.81, 127.69, 128.31, 125.52, 122.81 and 120.11 (q, J_{C-F} = 272.0 Hz), 125.18, 125.14, 125.10 and 125.06 (q, J_{C-F} = 3.7 Hz), 65.6, 23.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5; FTIR (film) ν 3335, 1616, 1411, 1327, 1167, 1126, 1068, 1016, 840, 726, 703 cm^{-1}; HRMS (EI) *m*/*z* calcd for $C_{17}H_{15}F_3O$ [M] 292.1075, found 292.1080.

*(S,E)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)benzonitrile (**8j**).* Yield of 239 mg (96%) starting from 437 mg of vinyl stannane **12a**; colorless oil; $[\alpha]_D^{25}$ −54.5 (*c* 0.84, $CHCl_3$) (98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.44−7.31 (m, 5H), 7.19−7.14 (m, 2H), 6.17 (d, *J* = 9.0 Hz, 1H), 4.40 (p, *J* = 9.0, 6.3 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 141.2, 138.2, 135.4, 132.2, 129.7, 128.8, 128.5, 128.1, 119.0, 111.2, 65.8, 23.8; FTIR (film) ν 3408, 1604, 1055, 837, 713, 549 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{15}NONa$ ([M + Na)$^+$] 272.1051, found 272.1052.

*(S,E)-1-(4-(3-Hydroxy-1-phenylbut-1-en-1-yl)phenyl)ethan-1-one (**8k**).* Yield of 211 mg (79%) starting from 437 mg of vinyl stannane **12a**; $[\alpha]_D^{24}$ −46.5 (*c* 2.6, $CHCl_3$) (98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91−7.81 (m, 2H), 7.44−7.28 (m, 5H), 7.20-−7.13 (m, 2H), 6.18 (d, *J* = 9.0 Hz, 1H), 4.41 (dq, *J* = 9.0, 6.3 Hz, 1H), 2.57 (s, 3H), 1.35 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 146.3, 141.6, 138.6, 136.0, 134.4, 129.6, 128.5, 128.3, 127.8, 127.5, 65.6, 26.6, 23.6; FTIR (film) ν 3410, 1681, 1602, 1360, 1270, 1055, 836, 709 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}O_2Na$ [(M + Na)$^+$] 289.1204, found 289.1206.

*Methyl (S,E)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)benzoate (**8l**).* Yield of 240 mg (85%) starting from 437 mg of vinyl stannane **12a**; $[\alpha]_D^{21}$ −35.0 (c 0.69, $CHCl_3$) (98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95−7.89 (m, 2H), 7.41−7.22 (m, 5H), 7.18−7.14 (m, 2H), 6.16 (d, *J* = 9.0 Hz, 1H), 4.39 (dq, *J* = 9.0, 6.3 Hz, 1H), 3.88 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 146.2, 141.5, 138.6, 134.4, 129.6, 129.5, 129.0, 128.4, 128.0, 127.7, 127.4, 65.6, 52.1, 23.6; FTIR (film) ν 3424, 1721, 1607, 1436, 1113, 1054, 854, 773, 704 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{18}O_3Na$ [(M + Na)$^+$] 305.1154, found 305.1146.

*(S,Z)-4-Phenyl-4-(p-tolyl)but-3-en-2-ol (**6a**).* Yield of 200 mg (98%) starting from 388 mg of vinyl stannane **12b**; $[\alpha]_D^{21}$ −47.7 (*c* 2.1, $CHCl_3$) (97% ee, HPLC R_t = 8.0 min); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 5H), 7.20−7.17 (m, 2H), 7.10−7.06 (m, 2H), 6.05 (d, *J* = 9.0 Hz, 1H), 4.45−4.36 (m, 1H), 2.39 (s, 3H), 1.33 (d, *J* = 6.3 Hz, 3H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{18}ONa$ [(M + Na)$^+$] 261.1255, found 261.1254; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 8.16 min (*S*-isomer) and 10.5 min (*R*-isomer).

*(S,Z)-4-(Naphthalen-2-yl)-4-phenylbut-3-en-2-ol (**6b**).* Yield of 123 mg (89%) starting from 243 mg of vinyl stannane **12c**; $[\alpha]_D^{22}$ −42.0 (*c* 0.57, $CHCl_3$) (98% ee, HPLC R_t = 11.05 min); ^1H NMR (400 MHz, $CDCl_3$) δ 7.93−7.84 (m, 3H), 7.78−7.75 (m, 1H), 7.58−

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7.51 (m, 2H), 7.32 (tdd, J = 6.0, 3.9, 1.8 Hz, 6H), 6.23 (d, J = 9.1 Hz, 1H), 4.50 (dq, J = 9.1, 6.3 Hz, 1H), 1.90 (s, 1H), 1.41 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.7, 136.9, 133.2, 132.9, 132.7, 128.6, 128.3, 128.1, 128.0, 127.9, 127.8, 127.70, 127.69, 126.4, 126.2, 65.9, 23.9; HPLC (rac) Chiralpak IB: 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 11.07 min (*S*-isomer) and 18.07 min (*R*-isomer).

*(S,Z)-4-(Naphthalen-1-yl)-4-phenylbut-3-en-2-ol (**6c**).* Yield of 21 mg (15%, after 3 days) starting from 245 mg of vinyl stannane **12d**; 63% purity (NMR with internal standard); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.81 (m, 3H), 7.76−7.65 (m, 1H), 7.57−7.50 (m, 2H), 7.36−7.28 (m, 6H), 6.20 (d, J = 9.1 Hz, 1H), 4.52 (dq, J = 9.1, 6.3 Hz, 1H), 1.91 (s, 1H), 1.43 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.3, 136.5, 133.3, 132.8, 132.6, 128.4, 128.3, 128.2, 128.0, 127.8 (×2), 127.7, 127.5, 126.4, 126.2, 65.8, 23.7; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{18}ONa$ [(M + Na)$^+$] 297.1255, found 297.1255.

*(S,Z)-4-(4-Methoxyphenyl)-4-phenylbut-3-en-2-ol (**6d**).* Yield of 451 mg (90%) starting from 920 mg of vinyl stannane **12e**; $[\alpha]_D^{23}$ −53.7 (c 0.7, $CHCl_3$) (97% ee, HPLC R_t = 11.2 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.22 (m, 5H), 7.14−7.07 (m, 2H), 6.95−6.88 (m, 2H), 6.02 (d, J = 9.0 Hz, 1H), 4.50−4.37 (m, 1H), 3.84 (s, 3H), 1.34 (d, J = 6.3 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 277.1204, found 227.1201; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min, R_t = 11.3 min (*S*-isomer) and 16.4 min (*R*-isomer).

*(S,Z)-4-(2-Methoxyphenyl)-4-phenylbut-3-en-2-ol (**6e**).* Yield of 105 (95%) starting from 201 mg of vinyl stannane **12g**; solid/oil; $[\alpha]_D^{21}$ −7 (c 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−6.98 (m, 9H), 6.21 (d, J = 9.1 Hz, 1H), 4.20 (dq, J = 9.1, 6.2 Hz, 1H), 3.75 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{17}H_{18}O_2Na$ [(M + Na)$^+$] 227.1204, found 227.1203.

*(S,Z)-4-(4-Fluorophenyl)-4-phenylbut-3-en-2-ol (**6f**).* Yield of 110 mg (93%) starting from 223 mg of vinyl stannane **12i**; $[\alpha]_D^{22}$ −45.5 (c 0.45, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.02 (m, 9H), 6.07 (d, J = 9.1 Hz, 1H), 4.41−4.29 (m, 1H), 1.34 (d, J = 6.3 Hz, 3H); HRMS (EI) m/z calcd for $C_{16}H_{15}OF$ [M] 242.1107, found 242.1112.

*(S,Z)-4-(2-Chlorophenyl)-4-phenylbut-3-en-2-ol (**6h**).* Yield of 125 mg (97%) starting from 235 mg of vinyl stannane **12h**; $[\alpha]_D^{23}$ −18.8 (c 0.77, $CHCl_3$) (97.2% ee); ^{1}H NMR (600 MHz, toluene-d_7, 80 °C) δ 7.20−7.15 (m, 2H), 7.08−6.83 (m, 7H), 6.12 (d, J = 8.8 Hz, 1H), 4.07 (p, J = 8.8, 6.2 Hz, 1H), 1.15 (d, J = 6.2 Hz, 3H); HRMS (EI) m/z calcd for $C_{16}H_{15}OCl$ [M] 258.0811, found 258.0800.

*(S,Z)-4-(3-Hydroxy-1-phenylbut-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**6m**).* Yield of 190 mg (96%) starting from 304 mg of vinyl stannane **12e**; colorless oil; $[\alpha]_D^{22}$ −28.6 (c 1.68, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76−7.72 (m, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.28−7.23 (m, 3H), 7.18−7.14 (m, 2H), 7.14−7.09 (m, 2H), 7.02−6.98 (m, 2H), 6.06 (d, J = 9.1 Hz, 1H), 4.28 (dq, J = 9.1, 6.3 Hz, 1H), 2.44 (s, 3H), 1.81 (s, 1H), 1.31 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 145.5, 141.3, 141.2, 138.3, 133.1, 132.5, 131.0, 129.8, 128.5, 128.3, 127.8, 127.5, 122.2, 65.6, 23.8, 21.7; FTIR (film) ν 3552, 3381, 1598, 1500, 1445, 1372, 1198, 1176, 1153, 1092, 867, 771, 696, 562, 552 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{22}O_4SNa$ [(M + Na)$^+$] 417.1134, found 417.1134.

Synthesis of Allyl Carbamates 9 and 11: General Method. To a solution of allyl alcohol **6** or **8** (1 mmol) in dry CH_2Cl_2 (5 mL) cooled to 0 °C was added trichloroacetyl isocyanate (1.3 mmol). The progress of the reaction was followed by TLC. After 30 min, the solvent was removed under reduced pressure. The residue was dissolved in MeOH (5 mL) and water (1 mL), and K_2CO_3 (4 mmol) was added. The progress of the reaction was followed by TLC. When the starting material was consumed, 5 mL of water was added, and the aqueous solution was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel.

*(S,E)-4-Phenyl-4-(p-tolyl)but-3-en-2-yl Carbamate (**11a**).* Yield of 215 mg (79%) starting from 231 mg of allyl alcohol **8a**; off-white solid; mp 103−104 °C; $[\alpha]_D^{24}$ −13.6 (c 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.02 (m, 9H), 6.01 (d, J = 9.0 Hz, 1H), 5.28 (dq, J = 9.0, 6.4 Hz, 1H), 4.52 (s, 2H), 2.32 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 143.6, 139.1, 138.7, 137.5, 129.5, 128.8, 128.3, 127.5, 127.4, 127.3, 70.3, 21.3, 21.1; FTIR (film) ν 3491, 3347, 3271, 1719, 1372, 1305, 1048, 817, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}NO_2Na$ [(M + Na)$^+$] 304.1313, found 304.1313.

*(S,Z)-4-Phenyl-4-(p-tolyl)but-3-en-2-yl Carbamate (**9a**).* Yield of 138 mg (73%) starting from 160 mg of allyl alcohol **6a**; white solid; mp 165−166 °C; $[\alpha]_D^{29}$ +8.8 (c 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 5H), 7.18 (d, J = 7.8 Hz, 2H), 7.11−7.07 (m, 2H), 6.01 (d, J = 9.0 Hz, 1H), 5.31 (dq, J = 9.0, 6.4 Hz, 1H), 4.57 (br s, 2H), 2.37 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 143.7, 141.8, 137.2, 136.0, 129.4, 129.0, 128.1, 128.0, 127.6, 127.5, 70.3, 21.3; FTIR (film) ν 3456, 3328, 3278, 1725, 1704, 1389, 1375, 1042, 1020, 766, 698, 500 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{19}NO_2Na$ [(M + Na)$^+$] 304.1313, found 304.1314.

*(S,E)-4-(3-(Carbamoyloxy)-1-phenylbut-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**11b**).* Yield of 395 mg (85%) starting from allyl alcohol **8e**; sticky solid; $[\alpha]_D^{23}$ −0.3 (c 0.77, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.40−7.27 (m, 5H), 7.15 (dd, J = 8.5, 6.5 Hz, 4H), 6.89−6.85 (m, 2H), 5.99 (d, J = 8.8 Hz, 1H), 5.23 (dq, J = 8.8, 6.4 Hz, 1H), 4.58 (s, 2H), 2.43 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 149.1, 145.3, 142.2, 140.4, 138.4, 132.5, 129.7, 129.4, 129.2, 128.5, 128.5, 128.4, 127.7, 122.0, 70.1, 21.7, 21.1; FTIR (film) ν 3495, 3397, 1725, 1597, 1500, 1373, 1200, 1178, 1154, 1093, 1051, 865, 755, 712, 655 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{23}NO_5SNa$ [(M + Na)$^+$] 460.1195, found 460.1186.

*(S,Z)-4-(3-(Carbamoyloxy)-1-phenylbut-1-en-1-yl)phenyl 4-Methylbenzenesulfonate (**9b**).* Yield of 172 mg (85%) starting from allyl alcohol **6m**; sticky solid; $[\alpha]_D^{23}$ +19.5 (c 1.13, $CHCl_3$) (96% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.27−7.25 (m, 3H), 7.18−7.11 (m, 4H), 7.00 (d, J = 8.3 Hz, 2H), 6.03 (d, J = 8.9 Hz, 1H), 5.18 (p, J = 8.9, 6.4 Hz, 1H), 2.43 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 149.0, 145.5, 142.2, 141.0, 138.0, 132.3, 130.8, 129.8, 129.1, 128.6, 128.3, 127.9, 127.3, 122.3, 69.8, 21.7, 21.2; FTIR (film) ν 3492, 3396, 3271, 1725, 1598, 1500, 1372, 1198, 1176, 1154, 1049, 864, 563 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{23}NO_5SNa$ [(M + Na)$^+$] 460.1195, found 460.1187.

*(S,E)-4-(4-Fluorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**11e**).* Yield of 220 mg (86%) starting from 218 mg of allyl alcohol **8f**; white solid; mp 84−85 °C; $[\alpha]_D^{20}$ +1.15 (c 1.15, $CHCl_3$) (96.8% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.17 (m, 7H), 7.01−6.92 (m, 2H), 5.99 (d, J = 8.9 Hz, 1H), 5.27 (dq, J = 8.9, 6.4 Hz, 1H), 4.73 (s, 2H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 and 161.2 (d, J_{C-F} = 247.1 Hz), 156.2, 142.7, 138.8, 137.72 and 137.68 (d, J_{C-F} = 3.2 Hz), 129.4, 129.1 and 129.0 (d, J_{C-F} = 8.0 Hz), 128.4, 128.1, 127.7, 115.1 and 114.9 (d, J_{C-F} = 21.4 Hz), 70.1, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.7; FTIR (film) ν 3497, 3347, 3197, 1720, 1508, 1373, 1231, 1049, 833, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2FNa$ [(M + Na)$^+$] 308.1063, found 308.1058.

*(S,Z)-4-(4-Fluorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**9e**).* Yield of 330 mg (72%) starting from 390 mg of allyl alcohol **6f**; white solid; mp 139−140 °C; $[\alpha]_D^{21}$ −0.66 (c 1.05, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.04 (m, 9H), 6.04 (d, J = 9.0 Hz, 1H), 5.27 (dq, J = 9.0, 6.4 Hz, 1H), 4.86 (s, 2H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5 and 161.0 (d, J_{C-F} = 246.6 Hz), 156.3, 142.7, 141.4, 134.90 and 134.86 (d, J_{C-F} = 3.5 Hz), 131.3 and 131.2 (d, J_{C-F} = 8.0 Hz), 128.7, 128.2, 127.8, 127.4, 115.4 and 115.2 (d, J_{C-F} = 21.4 Hz), 70.0, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.5; FTIR (film) ν 3597, 3345, 3129, 1718, 1602, 1508, 1373, 1222, 1049, 840, 766, 696 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2FNa$ [(M + Na)$^+$] 308.1063, found 308.1058.

*(S,E)-4-(4-Chlorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**11f**).* Yield of 48 mg (79%) starting from 52 mg of alcohol **8g**; $[\alpha]_D^{22}$ −5.6 (c 0.55, $CHCl_3$) (96.6% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.31 (m, 3H), 7.27−7.21 (m, 2H), 7.22−7.13 (m, 4H), 6.02 (d, J = 8.9

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Hz, 1H), 5.27 (dq, J = 8.9, 6.4 Hz, 1H), 4.61 (s, 2H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 142.5, 140.0, 138.5, 133.6, 129.4, 128.7, 128.4, 128.3, 127.7, 70.1, 21.2; FTIR (film) ν 3447, 3333, 3282, 3186, 1728, 1707, 1387, 1377, 1141, 1044, 1018, 826, 769, 756, 697, 547 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2ClNa$ [(M + Na)$^+$] 324.0767, found 324.0760.

*(S,Z)-4-(4-Chlorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**9f**).* Yield of 170 mg (63%) starting from 230 mg of allyl alcohol **6g**; white solid; mp 166−168 °C; $[\alpha]_D^{29}$ +19.6 (c 1.04, $CHCl_3$) (94% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 2H), 7.29−7.25 (m, 2H), 7.22−7.19 (m, 2H), 7.18−7.15 (m, 2H), 6.04 (d, J = 9.0 Hz, 1H), 5.26 (dq, J = 9.0, 6.4 Hz, 1H), 4.60 (s, 2H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 142.5, 141.1, 137.4, 133.6, 130.9, 128.8, 128.6, 128.2, 127.9, 127.4, 70.0, 21.2; FTIR (film) ν 3447, 3333, 3282, 3186, 1728, 1707, 1387, 1377, 1141, 1044, 1018, 826, 769, 756, 697, 547 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2ClNa$ [(M + Na)$^+$] 324.0767, found 324.0765.

*(S,E)-4-(2-Chlorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**11g**).* Yield of 125 mg (96%) starting from 111 mg of allyl alcohol **8h**; $[\alpha]_D^{22}$ +46.5 (c 0.58, $CHCl_3$) (97% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.19 (m, 9H), 5.76 (d, J = 9.1 Hz, 1H), 5.53 (dq, J = 9.1, 6.3 Hz, 1H), 4.66 (s, 2H), 1.41 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 141.7, 141.5, 138.6, 133.1, 132.3, 131.3, 129.9, 129.0, 128.7, 128.1, 127.6, 126.5, 69.6, 69.6, 21.1; FTIR (film) ν 3454, 3331, 3184, 1725, 1705, 1393, 1375, 1725, 1703, 1395, 1375, 1051, 1022, 762, 746, 698, 525 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2ClNa$ [(M + Na)$^+$] 324.0767, found 324.0759.

*(S,Z)-4-(2-Chlorophenyl)-4-phenylbut-3-en-2-yl Carbamate (**9g**).* Yield of 120 mg (86%) starting from 119 mg of allyl alcohol **6h**; $[\alpha]_D^{22}$ +4.4 (c 0.5, $CHCl_3$) (97.2% ee); ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.44−7.21 (m, 9H), 6.21 (d, J = 8.8 Hz, 1H), 5.16−5.06 (m, 1H), 4.61 (d, J = 8.0 Hz, 2H), 1.33 (d, J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 140.5, 139.4, 137.5, 133.6, 131.5, 129.6, 129.5, 129.2, 128.3, 127.8, 127.0, 126.5, 70.5, 20.4; FTIR (film) ν 3455, 3330, 3183, 1725, 1703, 1393, 1375, 1725, 1703, 1393, 1375, 1049, 1020, 762, 748, 694, 522 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_2ClNa$ [(M + Na)$^+$] 324.0767, found 324.0756.

*(S,E)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl Carbamate (**11h**).* Yield of 330 mg (90%) starting from 292 mg of alcohol **8i**; white solid; mp 85−86 °C; $[\alpha]_D^{23}$ +4.5 (c 0.78, $CHCl_3$) (97.4% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.50 (m, 2H), 7.43−7.31 (m, 5H), 7.22−7.18 (m, 2H), 6.10 (d, J = 8.8 Hz, 1H), 5.30 (dq, J = 8.8, 6.4 Hz, 1H), 4.59 (s, 2H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 142.8, 142.3, 140.7, 129.9, 130.2, 129.9, 129.6, 129.3 (q, J_{C-F} = 32 Hz), 129.3, 128.3, 128.0, 127.3, 125.40, 125.36, 125.32, 125.28 (q, J_{C-F} = 3.7 Hz), 127.9, 125.5, 122.8, 120.1 (q, J_{C-F} = 272 Hz), 69.9, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5; FTIR (film) ν 3500, 3348, 3187, 1721, 1616, 1374, 1326, 1168, 1125, 1067, 1016, 836, 704 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}F_3NO_2Na$ [(M + Na)$^+$] 358.1031, found 358.1022.

*(S,Z)-4-Phenyl-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl Carbamate (**9h**).* Yield of 206 mg (70%) starting from 250 mg of allyl alcohol **6i**; yellowish solid; mp 137−139 °C; $[\alpha]_D^{25}$ +17.3 (c 0.98, $CHCl_3$) (97.5% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 7.30−7.25 (m, 3H), 7.22−7.18 (m, 2H), 6.09 (d, J = 9.0 Hz, 1H), 5.22 (dq, J = 9.0, 6.4 Hz, 1H), 4.62 (br s, 2H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 142.8, 142.3, 140.7, 129.9, 129.3, 128.3, 128.0, 127.3, 125.3 (q, J_{C-F} = 3.7 Hz), 77.3, 77.0, 76.7, 69.9, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5; FTIR (film) ν 3464, 3330, 3276, 3184, 1725, 1705, 1617, 1399, 1377, 1325, 1165, 1125, 1065, 1022, 765, 696, 519 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}NO_2F_3Na$ [(M + Na)$^+$] 358.1031, found 358.1031.

*(S,E)-4-(4-Cyanophenyl)-4-phenylbut-3-en-2-yl Carbamate (**11i**).* Yield of 276 mg (94%) starting from 249 mg of alcohol **8i**; white solid; mp 114−115 °C; $[\alpha]_D^{23}$ −3.8 (c 1.05, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.51 (m, 2H), 7.43−7.29 (m, 5H), 7.22−7.16 (m, 2H), 6.13 (d, J = 8.8 Hz, 1H), 5.28 (dq, J = 8.8, 6.4 Hz, 1H), 4.71 (s, 2H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 146.0, 141.9, 137.7, 132.0, 131.4, 129.4, 128.7, 128.3, 127.9, 118.8, 111.1, 69.8, 21.0; FTIR (film) ν 3491, 3366, 3190, 2227, 1724, 1604, 1372, 1302, 1053, 836, 716 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}N_2O_2Na$ [(M + Na)$^+$] 315.1109, found 315.1110.

*(S,Z)-4-(4-Cyanophenyl)-4-phenylbut-3-en-2-yl Carbamate (**9i**).* Yield of 105 mg (69%) starting from 130 mg of alcohol **6j** white solid; mp 202−204 °C; $[\alpha]_D^{22}$ +66.1 (c 0.54, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.67 (m, 2H), 7.39−7.35 (m, 2H), 7.31−7.27 (m, 3H), 7.19−7.15 (m, 2H), 6.08 (d, J = 9.1 Hz, 1H), 5.19 (dq, J = 9.1, 6.4 Hz, 1H), 4.56 (s, 2H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 144.0, 142.0, 140.4, 132.2, 130.4, 129.6, 128.4, 128.2, 127.3, 118.7, 111.6, 69.6, 21.1; FTIR (film) ν 3462, 3324, 3281, 3182, 1721, 1701, 1620, 1604, 1389, 1375, 1363, 1140, 1040, 1048, 1021, 768, 701, 558, 491 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}N_2O_2Na$ [(M + Na)$^+$] 315.1109, found 315.1107.

*(S,E)-4-(4-Acetylphenyl)-4-phenylbut-3-en-2-yl Carbamate (**11j**).* Yield of 210 mg (94%) starting from 192 mg of alcohol **8k**; brown oil; $[\alpha]_D^{23}$ −8.8 (c 1.24, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.79 (m, 2H), 7.45−7.29 (m, 5H), 7.23−7.14 (m, 2H), 6.13 (d, J = 8.8 Hz, 1H), 5.27 (dq, J = 8.8, 6.4 Hz, 1H), 4.78 (s, 2H), 2.55 (s, 3H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 156.1, 146.1, 142.6, 138.2, 136.1, 130.5, 129.4, 128.5, 128.3, 127.8, 127.5, 69.9, 26.6, 21.1; FTIR (film) ν 3481, 3357, 3198, 1724, 1679, 1602, 1368, 1270, 1052, 709 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_3Na$ [(M + Na)$^+$] 332.1263, found 332.1260.

*(S,Z)-4-(4-Acetylphenyl)-4-phenylbut-3-en-2-yl Carbamate (**9j**).* Yield of 160 mg (86%) starting from 160 mg of allyl alcohol **6k** (Suzuki coupling product); brown oil; $[\alpha]_D^{22}$ +43.8 (c 0.8, $CHCl_3$) (95% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.96 (m, 2H), 7.35−7.32 (m, 2H), 7.30−7.25 (m, 3H), 7.22−7.18 (m, 2H), 6.08 (d, J = 9.0 Hz, 1H), 5.25 (dq, J = 9.0, 6.4 Hz, 1H), 4.58 (s, 2H), 2.62 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 155.9, 144.1, 142.7, 140.8, 136.3, 129.9, 129.0, 128.4, 128.3, 128.0, 127.3, 69.9, 26.6, 21.1; FTIR (film) ν 3476, 3357, 1722, 1682, 1604, 1371, 1360, 1268, 1051, 763 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_3Na$ [(M + Na)$^+$] 332.1263, found 332.1266.

*Methyl (S,E)-4-(3-(Carbamoyloxy)-1-phenylbut-1-en-1-yl)-benzoate (**11k**).* Yield of 210 mg (83%) starting from 220 mg of allyl alcohol **8l**; yellowish oil; $[\alpha]_D^{23}$ −6.9 (c 0.7, $CHCl_3$) (98% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.90 (m, 2H), 7.40−7.33 (m, 3H), 7.31−7.26 (m, 2H), 7.20−7.17 (m, 2H), 6.12 (d, J = 8.9 Hz, 1H), 5.29 (dq, J = 8.9, 6.4 Hz, 1H), 4.73 (s, 2H), 3.89 (s, 3H), 1.33 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 156.1, 146.0, 142.7, 138.3, 130.3, 129.5, 129.4, 129.2, 128.5, 127.8, 127.3, 70.0, 52.1, 21.1; FTIR (film) ν 3485, 3365, 1720, 1607, 1372, 1282, 1112, 1062, 772, 704 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_4Na$ [(M + Na)$^+$] 348.1212, found 348.1208.

*Methyl (S,Z)-4-(3-(Carbamoyloxy)-1-phenylbut-1-en-1-yl)-benzoate (**9k**).* Yield of 160 mg (77%) starting from 169 mg of allyl alcohol **6l** (Suzuki coupling product); yellowish oil; $[\alpha]_D^{23}$ +28.6 (c 0.79, $CHCl_3$) (92% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−8.03 (m, 2H), 7.33−7.28 (m, 2H), 7.28−7.23 (m, 3H), 7.22−7.15 (m, 2H), 6.07 (d, J = 9.0 Hz, 1H), 5.23 (dq, J = 9.0, 6.4 Hz, 1H), 4.77 (s, 2H), 3.91 (s, 3H), 1.32 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 156.2, 143.9, 142.7, 140.8, 129.7, 129.6, 129.3, 129.0, 128.3, 127.9, 127.3, 69.8, 52.1, 21.1; FTIR (film) ν 3468, 3366, 3198, 1721, 1607, 1437, 1372, 1285, 114, 1103, 1051, 764 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_4Na$ [M + Na$^+$] 348.1212, found 348.1211.

Ichikawa Rearrangement of Allyl Carbamates 9 and 11: General Method. To a solution of carbamate **9** or **11** (0.5 mmol) and Et_3N (3 mmol) in dry THF (10 mL) cooled to 0 °C was added TFAA (1 mmol), and the resulting mixture was slowly warmed to room temperature. The progress of the reaction was followed by TLC. When the starting material was consumed, dry MeOH (10 mL) and Bu_3SnOMe (0.05 mmol) were added, and the reaction mixture was left to stand overnight. After removal of solvents, the crude product was purified by column chromatography on silica gel.

*Methyl (S,E)-(1-Phenyl-1-(p-tolyl)but-2-en-1-yl)carbamate (**10a**).* Yield of 104 mg (78%) starting from 125 mg of carbamate **9a**; white solid; mp 122−124 °C; $[\alpha]_D^{24}$ −3.4 (c 0.95, $CHCl_3$) (98.4% ee, HPLC

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R_t = 9.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.05 (m, 9H), 6.46 (d, J = 15.6 Hz, 1H), 5.62 (s, 2H), 5.26−5.09 (m, 1H), 3.60 (s, 3H), 2.33 (s, 3H), 1.77 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 144.4, 141.4, 136.8, 134.4, 128.8, 128.0, 127.7, 127.7, 127.4, 127.1, 66.5, 51.8, 21.0, 17.8; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{21}NO_2Na$ [(M + Na)$^+$] 318.1470, found 318.1469.

*Methyl (R,E)-(1-Phenyl-1-(p-tolyl)but-2-en-1-yl)carbamate (ent-**10a**).* Yield of 144 mg (72%) starting from 190 mg of carbamate **11a**; white solid; mp 123−125 °C; $[\alpha]_D^{22}$ +3.1 (c 1.08, $CHCl_3$) (97.6% ee, HPLC R_t = 9.21 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.20 (m, 5H),7.16−7.05 (m, 4H), 6.46 (br d, J = 14.9 Hz, 1H), 5.62 (s, 2H), 5.26−5.09 (m, 1H), 3.60 (s, 3H), 2.33 (s, 3H), 1.77 (dd, J = 6.5, 1.7 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{19}H_{21}NO_2Na$ [(M + Na)$^+$] 318.1470, found 318.1468. HPLC (rac) Chiralcel OD-H, 5% i-PrOH in hexanes, 1 mL/min (254 nm), R_t = 8.74 min (R) and 9.52 min (S).

*(S,E)-4-(1-((Methoxycarbonyl)amino)-1-phenylbut-2-en-1-yl)-phenyl 4-Methylbenzenesulfonate (**10b**).* Yield of 88 mg (89%) starting from 96 mg of carbamate **9b**; waxy solid; $[\alpha]_D^{23}$ +0.29 (c 0.61, $CHCl_3$) (98% ee, HPLC R_t = 38.1 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.68 (m, 2H), 7.29 (ddt, J = 12.0, 6.7, 3.6 Hz, 5H), 7.20−7.11 (m, 4H), 6.97−6.91 (m, 2H), 6.38 (d, J = 15.6 Hz, 1H), 5.56 (s, 1H), 5.14 (dq, J = 15.5, 6.5 Hz, 1H), 3.57 (s, 3H), 2.44 (s, 3H), 1.75 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 148.8, 145.2, 143.7, 143.1, 134.2, 132.6, 129.6, 129.2, 128.4, 128.2, 128.1, 127.8, 127.5, 121.7, 66.4, 51.9, 21.6, 17.8; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{25}NO_5SNa$ [(M + Na)$^+$] 474.1351, found 474.1341; HPLC (rac) Chiralpak AS-H, 10% i-PrOH/hexane, 1 mL/min (254 nm), R_t = 38.05 min (S-isomer) and 46.89 min (R-isomer).

*(R,E)-4-(1-((Methoxycarbonyl)amino)-1-phenylbut-2-en-1-yl)-phenyl 4-Methylbenzenesulfonate (ent-**10b**).* Yield of 75 mg (79%) starting from 92 mg of carbamate **11b**; waxy solid; $[\alpha]_D^{23}$ −0.31 (c 0.64, $CHCl_3$) (96% ee, HPLC R_t = 46.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.69 (m, 2H), 7.34−7.24 (m, 5H), 7.20−7.11 (m, 4H), 6.97−6.91 (m, 2H), 6.38 (d, J = 15.6 Hz, 1H), 5.56 (s, 1H), 5.14 (dq, J = 15.6, 6.5 Hz, 1H), 3.57 (s, 3H), 2.44 (s, 3H), 1.75 (dd, J = 6.5, 1.7 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{25}H_{25}NO_5SNa$ [(M + Na)$^+$] 474.1351, found 474.1342; HPLC (rac) Chiralpak AS-H, 10% i-PrOH/hexane, 1 mL/min (254 nm), R_t = 38.05 min (S-isomer) and 46.89 min (R-isomer).

*Methyl (S,E)-(1-(4-Fluorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (**10e**).* Yield of 85 mg (81%) starting from 100 mg of carbamate **9d**; white solid; mp 94−95 °C; $[\alpha]_D^{22}$ +0.28 (c 0.73, $CHCl_3$) (97% ee, HPLC R_t = 11.7 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.18 (m, 7H),7.05−6.97 (m, 2H), 6.45 (d, J = 15.6 Hz, 1H), 5.61 (s, 1H), 5.18 (dq, J = 15.6, 6.5 Hz, 1H), 3.60 (s, 3H), 1.77 (d,J = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 144.1, 134.3, 129.7, 129.5, 128.7, 127.76, 127.66, 127.6, 114.9, 114.7, 66.4, 51.9, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.6; FTIR (film) ν 3443, 3337, 1737, 1507, 1447, 1239, 837, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}NO_2FNa$ [(M + Na)$^+$] 322.1219, found 322.1211; HPLC (rac) Chiralpak AS-H, 5% i-PrOH in hexanes, 1 mL/min (254 nm), R_t = 11.7 min (S-isomer) and 12.19 min (R-isomer).

*Methyl (R,E)-(1-(4-Fluorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (ent-**10e**).* Yield of 90 mg (86%) starting from 100 mg of carbamate **11d**; white solid; mp 93−94 °C; $[\alpha]_D^{22}$ −0.3 (c 0.8, $CHCl_3$) (98% ee, HPLC R_t = 12.06 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.18 (m, 7H),7.03−6.96 (m, 2H), 6.43 (d, J = 15.6 Hz, 1H), 5.59 (s, 1H), 5.18 (dq, J = 15.6, 6.5 Hz, 1H), 3.60 (s, 3H), 1.77 (d,J = 6.5 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}NO_2FNa$ [(M + Na)$^+$] 322.1219, found 322.1211; HPLC (rac) Chiralpak AS-H, 5% i-PrOH in hexanes, 1 mL/min (254 nm), R_t = 11.7 min (S-isomer) and 12.19 min (R-isomer).

*Methyl (S,E)-(1-(4-Chlorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (**10f**).* Yield of 80 mg (63%) starting from 121 mg of allyl carbamate **6g** (product of Suzuki coupling); white solid; mp 80−81 °C; $[\alpha]_D^{22}$−6.9 (c 1.09, $CHCl_3$) (94.6% ee, R_t = 28.2 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.15 (m, 9H), 6.41 (d, J = 15.6 Hz, 1H), 5.59 (s, 1H), 5.19 (dq, J = 15.6, 6.5 Hz, 1H), 3.60 (s, 3H), 1.77 (dd,J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 143.9, 142.7, 134.8, 134.1, 133.0, 129.3, 128.23, 128.19, 127.9, 127.7, 127.4, 66.3, 51.9, 17.8; FTIR (film) ν 3427, 3333, 1737, 1491, 1448, 1244, 1092, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}NO_2ClNa$ [(M + Na)$^+$] 338.0924, found 338.0926; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, flow 0.5 mL/min, det. 230 nm, R_t = 27.3 min (R-enantiomer) and 29.1 min (S-enantiomer).

*Methyl (R,E)-(1-(4-Chlorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (ent-**10f**).* Yield of 87% (84%) starting from 100 mg of allyl carbamate **11f**; $[\alpha]_D^{23}$ +7.8 (c 0.65, $CHCl_3$) (96.6% ee, HPLC R_t = 26.2 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.16 (m, 9H), 6.42 (br d, J = 15.6 Hz, 1H), 5.60 (s, 1H), 5.20 (dq, J = 15.6, 6.5 Hz, 1H), 3.60 (s, 3H), 1.77 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 143.9, 142.8, 134.8, 134.2, 133.1, 129.3, 128.23, 128.19, 127.8, 127.7, 127.5, 66.3, 51.7, 17.5; FTIR (film) ν 3427, 3333, 1737, 1491, 1448, 1244, 1092, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}NO_2ClNa$ [(M + Na)$^+$] 338.0924, found 338.0919; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, flow 0.5 mL/min, det. 230 nm, R_t = 27.3 min (R-enantiomer) and 29.1 min (S-enantiomer).

*Methyl (S,E)-(1-(2-Chlorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (**10g**).* Yield of 37 mg (65%) starting from 54 mg of allyl carbamate **9g**; $[\alpha]_D^{23}$ −25.3 (c 1.1, $CHCl_3$) (97% ee, HPLC R_t = 11.87 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.3, 2.2 Hz, 1H), 7.36−7.23 (m, 6H), 7.13−7.08 (m, 2H), 6.56 (br d, J = 15.6 Hz, 1H), 6.02 (s, 1H), 5.02 (dq, J = 15.6, 6.5 Hz, 1H), 3.58 (s, 3H), 1.75 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 142.9, 140.9, 133.9, 133.2, 131.7, 131.5, 128.9, 128.3, 127.7, 127.3, 126.8, 126.1, 66.5, 51.9, 17.8; FTIR (film) ν 3440, 3354, 1734, 1491, 1241, 1192, 998, 759, 703 cm^{-1}; HRMS (ESI-TOF) m/z $C_{18}H_{18}NO_2ClNa$ [(M + Na)$^+$] 338.0924, found 338.0919; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, 1 mL/min, R_t = 10 min (R-enantiomer) and 12 min (S-enantiomer).

*Methyl (R,E)-(1-(2-Chlorophenyl)-1-phenylbut-2-en-1-yl)-carbamate (ent-**10g**).* Yield of 80 mg (70%) starting from 111 mg of allyl carbamate **11g**; $[\alpha]_D^{23}$ +25.9 (c 0.91, $CHCl_3$) (96.6% ee, HPLC R_t = 10 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.57 (m, 1H), 7.37−7.25 (m, 6H), 7.13−7.08 (m, 2H), 6.57 (d, J = 15.6 Hz, 1H), 6.03 (s, 1H), 5.03 (dq, J = 15.6, 6.5 Hz, 1H), 3.59 (s, 3H), 1.76 (dd, J = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 142.9, 140.9, 133.9, 133.2, 131.7, 131.5, 128.9, 128.3, 127.7, 127.3, 126.8, 126.1, 66.5, 51.9, 17.8; FTIR (film) ν 3441, 3353, 1734, 1491, 1241, 1193, 999, 759, 703 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{18}NO_2ClNa$ [(M + Na)$^+$] 338.0924, found 338.0916; HPLC (rac) Chiralpak IB, 1% i-PrOH in hexanes, 1 mL/min, R_t = 10 min (R-enantiomer) and 12 min (S-enantiomer).

*Methyl (S,E)-(1-Phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)carbamate (**10h**).* Yield of 90 mg (86%) starting from 100 mg of carbamate **9h**; white solid; mp 71.5−72.5 °C; $[\alpha]_D^{21}$ +0.66 (c 0.8, $CHCl_3$) (97.5% ee, HPLC R_t = 8.47 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H),7.36−7.23 (m, 3H),7.20−7.15 (m, 2H), 6.43 (d, J = 15.6 Hz, 1H), 5.65 (s, 1H), 5.24 (dq, J = 15.6, 6.6 Hz, 1H), 3.61 (s, 3H), 1.79 (dd,J = 6.6, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 148.1, 143.6, 133.9, 129.8, 129.5, 129.2 and 128.8 (q, J_{C-F} = 32.6 Hz), 129.1, 128.32, 128.28, 128.2, 127.7, 127.6, 128.3, 125.5, 122.8 and 120.1 (q, J_{C-F} = 272 Hz), 125.1, 125.04, 125.00 and 124.97 (q, J_{C-F} = 3.8 Hz), 66.5, 52.0, 17.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.5; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{18}F_3NO_2Na$ [(M + Na)$^+$] 372.1187, found 372.1184; HPLC (rac) Chiralcel OD-H, 5% i-PrOH in hexanes, 1 mL/min (254 nm), R_t = 7.96 min (R-isomer) and 8.59 min (S-isomer).

*Methyl (R,E)-(1-Phenyl-1-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)carbamate (ent-**10h**).* Yield of 90 mg (86%) starting from 100.6 mg of carbamate **11h**; white solid; mp 71−72 °C; $[\alpha]_D^{21}$ −0.7 (c 1.0, $CHCl_3$) (97.4% ee, HPLC R_t = 7.86 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.35−7.24 (m, 3H), 7.19−7.14 (m, 2H), 6.43 (d, J = 15.6 Hz, 1H), 5.65 (s, 1H), 5.24 (dq, J = 15.6, 6.5 Hz, 1H), 3.61 (s, 3H), 1.79 (dd, J = 6.6, 1.7 Hz, 3H); HRMS (ESI-TOF) m/z calcd for $C_{19}H_{18}F_3NO_2Na$ [(M + Na)$^+$] 372.1187, found 372.1183; HPLC (rac) Chiralcel OD-H, 5% i-PrOH

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in hexanes, 1 mL/min (254 nm), R_t = 7.96 min (*R*-isomer) and 8.59 min (*S*-isomer).

*Methyl (S,E)-(1-(4-Cyanophenyl)-1-phenylbut-2-en-1-yl)-carbamate (**10i**).* Yield of 75 mg (72%) starting from carbamate **9i**; waxy solid; $[\alpha]_D^{23}$ −7.1 (*c* 1.2, $CHCl_3$) (98% ee, HPLC R_t = 36.2 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35−7.23 (m, 3H), 7.15−7.10 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.65 (s, 1H), 5.24 (dq, *J* = 15.6, 6.5 Hz, 1H), 3.60 (s, 3H), 1.79 (dd, *J* = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 143.2, 133.7, 131.9, 129.1, 128.6, 128.4, 127.8, 127.6, 125.2, 118.8, 111.0, 66.5, 52.0, 17.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{18}N_2O_2Na$ [(M + Na)$^+$] 329.1266, found 329.1262.

*Methyl (R,E)-(1-(4-Cyanophenyl)-1-phenylbut-2-en-1-yl)-carbamate (ent-**10i**).* Yield of 92 mg (88%) starting from 100 mg of carbamate **11i**; waxy solid; $[\alpha]_D^{23}$ +7.8 (*c* 0.87, $CHCl_3$) (98% ee, HPLC R_t = 35.19 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.60 (m, 2H), 7.48−7.44 (m, 2H), 7.35−7.28 (m, 3H), 7.15−7.11 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.66 (s, 1H), 5.24 (dq, *J* = 15.6, 6.6 Hz, 1H), 3.60 (s, 3H), 1.79 (dd, *J* = 6.6, 1.7 Hz, 3H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{19}H_{18}N_2O_2Na$ [(M + Na)$^+$] 329.1266, found 329.1263; HPLC (rac) Chiralpak AS-H, 5% *i*-PrOH in hexanes, 1 mL/min (254 nm), R_t = 32.06 min (*S*-isomer) and 35.81 min (*R*-isomer).

*Methyl (S,E)-(1-(4-Acetylphenyl)-1-phenylbut-2-en-1-yl)-carbamate (**10j**).* Yield of 50 mg (77%) starting from 62 mg of carbamate **9j**; yellowish sticky oil; $[\alpha]_D^{23}$ −8.7 (*c* 1.0, $CHCl_3$) (98% ee, HPLC R_t = 60 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.90 (m, 2H), 7.43−7.39 (m, 2H), 7.34−7.15 (m, 5H), 6.42 (br d, *J* = 15.5 Hz, 1H), 5.66 (s, 1H), 5.23 (dq, *J* = 15.5, 6.5 Hz, 1H), 3.60 (s, 3H), 2.59 (s, 3H), 1.78 (dd, *J* = 6.5, 1.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 149.4, 143.7, 135.9, 133.9, 129.0, 128.3, 128.1, 128.0, 127.7, 127.6, 125.3, 66.6, 52.0, 26.6, 17.9; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}NO_3Na$ [(M + Na)$^+$] 346.1419, found 346.1417; HPLC (rac) Chiralcel OJ-H, 7% *i*-PrOH/hexanes, 1 mL/min (254 nm), R_t = 61.4 min (*S*-isomer) and 108.1 min (*R*-isomer).

*Methyl (R,E)-(1-(4-Acetylphenyl)-1-phenylbut-2-en-1-yl)-carbamate (ent-**10j**).* Yield of 118 mg (87%) starting from 130 mg of carbamate **11j**; yellowish sticky oil; $[\alpha]_D^{23}$ +8.8 (*c* 1.09, $CHCl_3$) (98% ee, HPLC R_t = 107 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.34−7.14 (m, 5H), 6.44 (br d, *J* = 15.3 Hz, 1H), 5.71 (br s, 1H), 5.29−5.19 (m, 1H), 3.60 (s, 3H), 2.59 (s, 3H), 1.79 (dd, *J* = 6.5, 1.6 Hz, 3H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}NO_3Na$ [(M + Na)$^+$] 346.1419, found 346.1413; HPLC (rac) Chiralcel OJ-H, 7% *i*-PrOH/hexanes, 1 mL/min (254 nm), R_t = 61.4 min (*S*-isomer) and 108.1 min (*R*-isomer).

*Methyl (S,E)-4-(1-((Methoxycarbonyl)amino)-1-phenylbut-2-en-1-yl)benzoate (**10k**).* Yield of 65 mg (80%) starting from 78 mg of carbamate **9j**; yellowish sticky oil; $[\alpha]_D^{23}$ −7.0 (*c* 0.72, $CHCl_3$) (98% ee, HPLC R_t = 19.62 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 2H), 7.30−7.27 (m, 2H), 7.24−7.04 (m, 5H), 6.34 (d, *J* = 15.1 Hz, 1H), 5.59 (s, 1H), 5.18−5.07 (m, 1H), 3.81 (s, 3H), 3.50 (s, 3H), 1.68 (dd, *J* = 6.5, 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 149.3, 143.8, 134.0, 129.4, 129.0, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 66.6, 52.0, 52.0, 17.9; FTIR (film) ν 3356, 1725, 1493, 1437, 1281, 1245, 1190, 1113, 758, 704 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}NO_4Na$ [(M + Na)$^+$] 362.1368, found 362.1360; HPLC (rac) Chiralpak AS-H, 5% *i*-PrOH/hexanes, 1 mL/min (254 nm), R_t = 17.39 min (*R*-isomer) and 19.49 min (*S*-isomer).

*Methyl (R,E)-4-(1-((Methoxycarbonyl)amino)-1-phenylbut-2-en-1-yl)benzoate (ent-**10k**).* Yield of 101 mg (88%) starting from 111 mg of carbamate **11j**; yellowish sticky oil; $[\alpha]_D^{23}$ +6.9 (*c* 0.75, $CHCl_3$) (98% ee, HPLC R_t = 17.24 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.87 (m, 2H), 7.30−7.27 (m, 2H), 7.24−7.04 (m, 5H), 6.34 (d, *J* = 15.1 Hz, 1H), 5.59 (s, 1H), 5.18−5.07 (m, 1H), 3.81 (s, 3H), 3.50 (s, 3H), 1.68 (dd, *J* = 6.5, 1.6 Hz, 3H); HRMS (ESI-TOF) *m*/*z* calcd for $C_{20}H_{21}NO_4Na$ [(M + Na)$^+$] 362.1368, found 362.1365; HPLC (rac) Chiralpak AS-H, 5% *i*-PrOH/hexanes, 1 mL/min (254 nm), R_t = 17.39 min (*R*-isomer) and 19.49 min (*S*-isomer).

Synthesis of Amino Acid Esters 13 and *ent*-13: General Method. Ozone was passed through a solution of carbamate (0.5 mmol) in dry CH_2Cl_2 (20 mL) cooled to −78 °C until the solution turned blue. Then, excess ozone was removed by bubbling oxygen through the mixture. After the addition of Me_2S (4 mL), the resulting mixture was warmed to room temperature and stirred for 1 h. After that, the solvent was removed under reduced pressure. The residue was dissolved in *t*-BuOH/H_2O (4:1 v/v, 15 mL) followed by the addition of $NaH_2PO_4{\cdot}H_2O$ (364 mg, 2.5 mmol), 2-methyl-2-butene (230 μL), and $NaClO_2$ (80% purity, 304 mg, 2.5 mmol). The resulting mixture was stirred overnight. Next, the solvent was removed; the crude amino acid was dissolved in dry MeOH, and (trimethylsilyl)-diazomethane (3 equiv, 2 M soln in Et_2O) was added slowly. When the reaction was complete, the solvent was removed, and the crude product was purified by flash column chromatography.

*Methyl (S)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(p-tolyl)-acetate (**13a**).* Yield of 66 mg (88%) starting from 71 mg of allylamine **13a**; $[\alpha]_D^{23}$ +3.8 (*c* 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.41 (m, 2H), 7.37−7.27 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 3.75 (s, 3H), 3.58 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 154.8, 139.3, 137.7, 136.3, 128.7, 128.4, 128.3, 127.9, 127.8, 69.4, 53.4, 52.0, 21.0; FTIR (film) ν 3411, 1730, 1496, 1262, 1036, 736, 701 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}NO_4Na$ [(M + Na)$^+$] 336.1212, found 336.1219

*Methyl (R)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(p-tolyl)-acetate (ent-**13a**).* Yield of 43 mg (81%) starting from 50 mg of allylamine *ent*-**10a**; $[\alpha]_D^{23}$ −3.6 (*c* 1.0, $CHCl_3$); HRMS (ESI-TOF) *m*/*z* calcd for $C_{18}H_{19}NO_4Na$ [(M + Na)$^+$] 336.1212, found 336.1214.

*Methyl (S)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(4-(tosyloxy)phenyl)acetate (**13b**).* Yield of 34 mg (80%) starting from 40.6 mg of allylamine **10b**; waxy solid; $[\alpha]_D^{22}$ +8.7 (*c* 1.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.70 (m, 2H), 7.40−7.28 (m, 9H), 7.01−6.93 (m, 2H), 6.43 (s, 1H), 3.74 (s, 3H), 3.56 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 155.4, 149.1, 145.4, 138.9, 137.9, 136.5, 132.6, 130.0, 129.8, 128.5, 128.2, 128.1, 121.6, 69.1, 53.6, 52.1, 21.7; FTIR (film) ν 3398, 1730, 1500, 1373, 1263, 1179, 1156, 867, 566, 552 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{23}NO_7SNa$ [(M + Na)$^+$] 492.1093, found 492.1108.

*Methyl (R)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(4-(tosyloxy)phenyl)acetate (ent-**13b**).* Yield of 58 mg (82%) starting from 67.7 mg of allylamine *ent*-**10b**; waxy solid; $[\alpha]_D^{22}$ −8.4 (*c* 1.09, $CHCl_3$); HRMS (ESI-TOF) *m*/*z* calcd for $C_{24}H_{23}NO_7SNa$ [(M + Na)$^+$] 492.1093, found 492.1100

*Methyl (S)-2-(4-Fluorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (**13c**).* Yield of 65 mg (89%) starting from 69 mg of allylamine **10e**; $[\alpha]_D^{23}$ +0.5 (*c* 1.39, $CHCl_3$) (98% ee, HPLC R_t = 36.5 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.31 (m, 7H), 7.06−6.98 (m, 2H), 6.50 (s, 1H), 3.75 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 163.4 and 161.0 (d, J_{C-F} = 247.5 Hz), 154.7, 139.0, 134.93 and 134.90 (d, J_{C-F} = 3.5 Hz), 130.5 and 130.4 (d, J_{C-F} = 8.2 Hz), 128.2, 128.1 (×2), 114.8 and 114.6 (d, J_{C-F} = 21.6 Hz), 69.1, 53.5, 52.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.5; FTIR (film) ν 3408, 1729, 1508, 1263, 1233, 1035, 701 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}NO_4FNa$ [(M + Na)$^+$] 340.0961, found 340.0967; HPLC (rac) Chiralpak IB, 1% *i*-PrOH in hexanes, 1 mL/min, R_t = 34.5 min (*R*-isomer) and 36.7 min (*S*-isomer).

*Methyl (R)-2-(4-Fluorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (ent-**13c**).* Yield of 60 mg (83%) starting from 72 mg of allylamine *ent*-**10e**; $[\alpha]_D^{23}$ −0.7 (*c* 1.72, $CHCl_3$) (98% ee); HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}NO_4FNa$ [(M + Na)$^+$] 340.0961, found 340.0963.

*Methyl (S)-2-(4-Chlorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (**13d**).* Yield of 26 mg (87%) starting from 28.4 mg of allylamine **10f**; $[\alpha]_D^{23}$ +10.4 (*c* 1.18, $CHCl_3$) (94.3% ee, HPLC R_t = 11.11 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.28 (m, 9H), 6.47 (s, 1H), 3.75 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 156.9, 142.4, 138.8, 137.6, 133.9, 130.1, 128.2, 128.2, 128.0, 69.1, 53.6, 52.1; FTIR (film) ν 3406, 1731, 1493, 1262, 1013, 701 cm^{-1}; HRMS (ESI-TOF) *m*/*z* calcd for $C_{17}H_{16}NO_4ClNa$ [(M + Na)$^+$] 356.0666, found 356.0660.

*Methyl (R)-2-(4-Chlorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (ent-**13d**).* Yield of 20 mg (85%) starting from 22 mg of allylamine *ent*-**10f**; $[\alpha]_D^{22}$ −10.7 (*c* 1.68, $CHCl_3$) (96.8% ee,

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HPLC R_t = 14.53 min); HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_4ClNa$ [(M + Na)$^+$] 356.0666, found 356.0663.

*Methyl (S)-2-(2-Chlorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (**13e**).* Yield of 20 mg (75%) starting from 25 mg of allylamine **10g**; $[\alpha]_D^{21}$ +3.72 (c 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.07 (m, 9H), 6.78 (s, 1H), 3.75 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 154.4, 137.4, 136.3, 133.8, 133.5, 130.2, 129.4, 128.35, 128.28, 128.1, 125.4, 68.8, 53.7, 52.1; FTIR (film) ν 3416, 1731, 1496, 1255, 1036, 747 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_4ClNa$ [(M + Na)$^+$] 356.0666, found 356.0663.

*Methyl (R)-2-(2-Chlorophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (ent-**13e**).* Yield of 24 mg (69%) starting from 32 mg of allylamine *ent*-**10g**; $[\alpha]_D^{23}$ −3.89 (c 0.49, $CHCl_3$); HRMS (ESI-TOF) m/z calcd for $C_{17}H_{16}NO_4ClNa$ [(M + Na)$^+$] 356.0666, found 356.0664.

*Methyl (S)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(4-(trifluoromethyl)phenyl)acetate (**13f**).* Yield of 72 mg (85%) starting from 80.4 mg of allylamine **10h**; $[\alpha]_D^{23}$ +9.0 (c 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.55 (m, 4H), 7.38−7.33 (m, 5H), 6.52 (s, 1H), 3.77 (s, 3H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 154.7, 142.9, 138.6, 130.4, 130.1, 129.8 and 129.5 (q, J_{C-F} = 32.2 Hz), 129.1, 128.34, 128.29, 128.09, 128,06, 125.4, 122.7 and 119.9 (q, J_{C-F} = 271 Hz), 124.83, 124.80, 124.76 and 124.72 (q, J_{C-F} = 3.7 Hz), 69.4, 53.7, 52.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.7; FTIR (film) ν 3411, 1731, 1496, 1328, 1265, 1168, 1125, 1071, 1016, 701 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}NO_4F_3Na$ [(M + Na)$^+$] 390.0929, found 390.0938.

*Methyl (R)-2-((Methoxycarbonyl)amino)-2-phenyl-2-(4-(trifluoromethyl)phenyl)acetate (ent-**13f**).* Yield of 70 mg (86%) starting from 80.4 mg of allylamine *ent*-**10h**; $[\alpha]_D^{23}$ −8.8 (c 1.04, $CHCl_3$); HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}NO_4F_3Na$ [(M + Na)$^+$] 390.0929, found 390.0938.

*Methyl (S)-2-(4-Cyanophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (**13g**).* Yield of 26 mg (80%) starting from 31 mg of allylamine **10i**; $[\alpha]_D^{23}$ +23.0 (c 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.61 (m, 2H), 7.59−7.54 (m, 2H), 7.40−7.30 (m, 5H), 6.47 (s, 1H), 3.78 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 154.8, 144.3, 138.2, 131.6, 129.5, 128.55, 128.48, 127.9, 118.5, 111.7, 69.4, 53.8, 52.3; FTIR (film) ν 3400, 1730, 1496, 1264, 1056, 1035, 1014, 737, 701 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}N_2O_4Na$ [(M + Na)$^+$] 347.1008, found 347.1010.

*Methyl (R)-2-(4-Cyanophenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (ent-**13g**).* Yield of 77 mg (88%) starting from 83 mg of allylamine *ent*-**10i**; $[\alpha]_D^{23}$ −23.6 (c 1.7, $CHCl_3$); HRMS (ESI-TOF) m/z calcd for $C_{18}H_{16}N_2O_4Na$ [(M + Na)$^+$] 347.1008, found 347.1011.

*Methyl (S)-2-(4-Acetylphenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (**13h**).* Yield of 36 mg (81%) starting from 42 mg of allylamine **10j**; $[\alpha]_D^{23}$ +18.2 (c 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.89 (m, 2H), 7.58−7.49 (m, 2H), 7.41−7.32 (m, 5H), 6.52 (s, 1H), 3.76 (s, 3H), 3.58 (s, 3H), 2.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 171.8, 154.7, 144.2, 138.5, 136.4, 128.9, 128.29, 128.25, 128.1, 127.8, 69.5, 53.7, 52.2, 26.6; FTIR (film) ν 3406, 3355, 1729, 1684, 1495, 2853, 1729, 1684, 1495, 1449, 1360, 1266, 1055, 1035, 1014, 736, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_3Na$ [(M + Na)$^+$] 364.1161, found 364.1167.

*Methyl (R)-2-(4-Acetylphenyl)-2-((methoxycarbonyl)amino)-2-phenylacetate (ent-**13h**).* Yield of 90 mg (91%) starting from 94 mg of allylamine *ent*-**10j**; $[\alpha]_D^{23}$ −18.4 (c 2.0, $CHCl_3$); HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_5Na$ [(M + Na)$^+$] 364.1161, found 364.1163.

*Methyl (S)-4-(2-Methoxy-1-((methoxycarbonyl)amino)-2-oxo-1-phenylethyl)benzoate (**13i**).* Yield of 45 mg (90%) starting from 48 mg of allylamine **10k**; $[\alpha]_D^{22}$ +16.3 (c 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.40−7.30 (m, 5H), 6.51 (s, 1H), 3.90 (s, 3H), 3.75 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 166.7, 154.7, 144.0, 138.6, 129.6, 129.1, 128.7, 128.2, 128.23, 128.20, 69.5, 53.6, 52.2, 52.1; FTIR (film) ν 3357, 1726, 1496, 1282, 1265, 1112, 702 cm^{-1}; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_6Na$ [(M + Na)$^+$] 380.1110, found 380.1110; HPLC (rac) Chiralpak IB, 10% *i*-PrOH in hexanes, 1 mL/min (240 nm), R_t = 30.21 min (*R*-enantiomer) and 33.13 min (*S*-enantiomer).

*Methyl (R)-4-(2-Methoxy-1-((methoxycarbonyl)amino)-2-oxo-1-phenylethyl)benzoate (ent-**13i**).* Yield of 77 mg (91%) starting from 81 mg of allylamine *ent*-**10k**; $[\alpha]_D^{23}$ −16.4 (c 0.8, $CHCl_3$); HRMS (ESI-TOF) m/z calcd for $C_{19}H_{19}NO_6Na$ [(M + Na)$^+$] 380.1110, found 380.1117.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00475.

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

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Notes

The authors declare no competing financial interest.

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