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Exploring the Steric and Electronic Factors Governing the Regio- and Enantioselectivity of the Pd-Catalyzed Decarboxylative Generation and Allylation of 2-Azaallyl Anions

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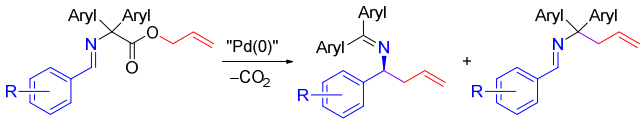
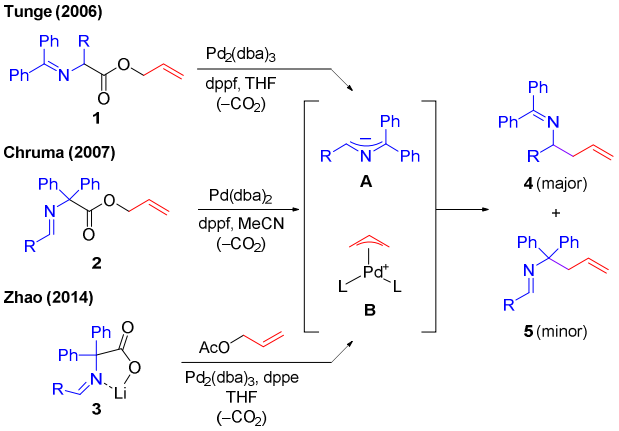


ABSTRACT: The impact of the steric and electronic factors in both the para-substituted benzaldimine and 2,2-diarylglycine components on the regioselectivity and enantioselectivity of the palladium-catalyzed decarboxylative allylation of allyl 2,2-diarylglycinate aryl imines was explored. These studies revealed that using 2,2-di(2-methoxyphenyl)glycine as the amino acid linchpin allowed for the exclusive synthesis of the desired homoallylic benzophenone imine regioisomers, independent of the nature of the imine moiety, in typically high yields. The resulting enantiomeric ratios, however, are slightly decreased in comparison to the transformations involving the corresponding allyl 2,2-diphenylglycinate imines, but this is more than balanced out by the increases in yield and regioselectivity. Overall, these studies suggest a general strategy for the highly regioselective functionalization of 2-azaallyl anions.

INTRODUCTION

For over a century, the 2-azaallyl anion has attracted significant attention as a nucleophilic imine umpolung.[1] A unifying concern for such processes is controlling the regioselectivity and potential enantioselectivity of the key C–C bond-forming step. Traditionally, 2-azaallyl anions are generated by deprotonation of the conjugate acid with strong amide bases,[2] though very recent reports indicate that such a tactic can lead to concomitant formation of 2-azaallyl radicals.[3] Decarboxylation is a relatively recent alternative strategy for the generation of 2-azaallyl anions with at least two aromatic substituents (a.k.a. semi-stabilized 2-azaallyl anions).[4] For example, Burger and Tunge disclosed a palladium-catalyzed decarboxylative generation and allylation of semi-stabilized 2-azaallyl anions from the allyl esters of various α-benzophenonimino acids (**1**, Scheme 1).[4a] Not long after, our group reported a complementary strategy starting from allyl diphenylglycinate imines (**2**);[4b] an asymmetric variant of this transformation using the chiral ligand (*S,S*)-*f*-binaphane[5] was reported much later.[4c] Zhao and co-workers advanced an "intermolecular" modification starting from lithium diphenylglycinate imines (**3**), several of which are stable complexes in protic solvents but decarboxylate readily upon dissolution in aprotic coordinating media.[4d] Under otherwise identical conditions, all three approaches afford essentially identical ratios of regioisomeric products **4** and **5**, strongly indicating that all three transformations proceed via the same delocalized 1,1-diphenyl-2-azaallyl anion (**A**) and cationic π-allylPd(II) (**B**) intermediates. Previous

Scheme 1. Complementary Methods for the Pd-Catalyzed Decarboxylative Generation and Allylation of 2-Azaallyl Anions

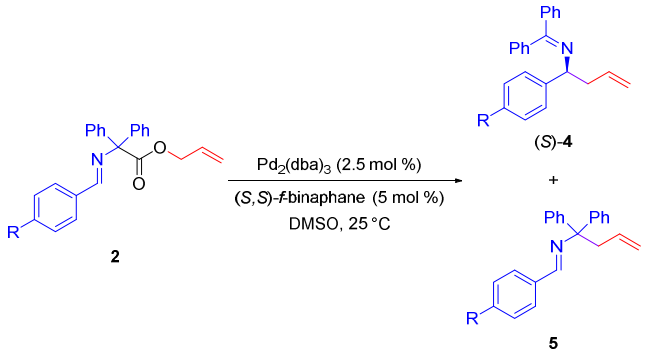


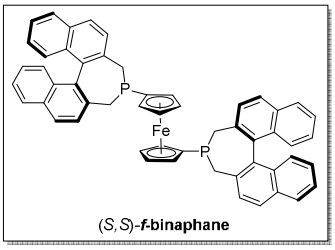
mechanistic studies revealed a positive linear Hammett correlation between the regioisomeric ratio [rr, log(**4**/**5**)] and the Hammett resonance constant (σ^-_p)[6] for the Pd-catalyzed decarboxylative allylation (DcA) of imino esters **2** in which the R groups were various *para*-substituted phenyl moieties.[7] That is to say that electron-deficient aromatic R groups demonstrated a significantly higher-to-exclusive preference for homoallylic imines **4** over aldimines **5**, whereas electron-rich R groups afforded only modest preferences for ketimines **4**. A roughly linear positive Hammett correlation was also observed for the enantiomeric ratio (er) values of the resulting benzophenone imines (*S*)-**4** in the asymmetric Pd-catalyzed DcA of allyl imino esters **2**,[4c] though this relationship appeared to be complicated by steric interactions between the R groups and the chiral ligand. Herein is disclosed a more detailed investigation into the steric and electronic factors governing both the regio- and enantioselectivity for the Pd-catalyzed DcA of allyl 2,2-diarylglycinate imines. These studies reveal that switching the amino acid linchpin to 2,2-di(2-methoxyphenyl)glycine completely solves the regioselectivity issue, affording the desired ketimines as the sole products in higher isolated yields compared to the 2,2-diphenylglycine analogs. While the enantioselectivities of the Pd-catalyzed DcAs suffered slight but general decreases upon switching to 2,2-di(2-methoxyphenyl)-glycine as the linchpin amino acid, the enatiopurity of the final products could be enriched by single recrystallization. Overall, these studies suggest a general strategy for the highly regioselective functionalization of semi-stabilized 2-azaallyl anions.

RESULTS AND DISCUSSION

Initial reports on the racemic Pd-catalyzed DcA of diphenylglycinate imino esters **2** using $Pd(dba)_2$ (10 mol %) and dppf (10 mol %) in MeCN revealed a strong positive linear Hammett correlation between regioselectivity [log(**4**/**5**)] and the Hammett resonance coefficient for *para* substituents (σ^-_p).[4b,7] Later studies using the chiral ligand (*S,S*)-*f*-binaphane in DMSO showed a much rougher positive linear correlation between enantioselectivity {log[(*S*)-**4**/(*R*)-**4**]} and σ^-_p for electron-withdrawing or electron-neutral R groups (Table 1, **2a**, **2b**, **2c**, **2f**, and **2h**), but with an apparent inflection point at **2h** (R = H) and a negative linear correlation for R groups with negative σ^-_p values, such as **2i** (R = F) and **2l** (R = Me).[4c] Inflection points in Hammett plots typically indicate a change in mechanism, but with regard to enantioselectivity it can also signify that a much more complicated relationship between both electronic and steric factors governs asymmetric induction.[8] If there is a significant change in the mechanistic pathway for the asymmetric DcA of imino esters **2** upon switching from electron-withdrawing to electron-donating *para* substituents, then an inflection point would also be expected in the Hammett plot for regioselectivity. While it was noted that strongly electron-withdrawing substituents (**2a-c**) only provided the corresponding benzophenone imines (**4a-c**), the regioselectivities for the asymmetric DcA of other α-imino esters **2**, regrettably, were not determined in our previous study.[4c]

Table 1. Regio- and Enantioselectivity for the Pd-Catalyzed Asymmetric DcA of Imino Esters 2





entry	R	σ^-_p [a]	v^b	rr (**4:5**)[c]	er (*S*:*R*)[d]
1	NO_2 (**2a**)	1.27	*NA*	>20:1[e]	94.7:5.3[e]
2	CN (**2b**)	1.00	*NA*	>20:1[e]	93.5:6.5[e]
3	CO_2Me (**2c**)	0.75	*NA*	>20:1[e]	93.9:6.1[e]
4	CF_3 (**2d**)	0.65	0.91	>20:1	88.9:11.1
5	I (**2e**)	0.27	0.78	15.5:1	87.1:12.9
6	Br (**2f**)	0.25	0.65	14.1:1	90.2:9.8[e]
7	Cl (**2g**)	0.19	0.55	10.5:1	86.3:13.7
8	H (**2h**)	0.00	0.00	7.2:1	86.2:13.8[e]
9	F (**2i**)	-0.03	0.27	5.4:1	86.9:13.1[e]
10	*i*-Bu (**2j**)	-0.12[f]	0.98	3.3:1	83.9:16.1
11	*t*-Bu (**2k**)	-0.13	1.24	2.9:1	79.7:20.3
12	Me (**2l**)	-0.17	0.52	2.9:1	89.5:10.5[e]
13	Et (**2m**)	-0.19	0.56	3.0:1	82.7:17.3
14	MeO (**2n**)	-0.26	*NA*	1.7:1	82.7:17.3

[a]Hammett resonance coefficient for *para* substituent (ref 6). [b]Charton steric coefficient (ref 9). [c]Determined by ^{1}H NMR analysis of the crude reaction mixture; average of three runs. [d]Determined by chiral HPLC analysis; average of three runs. [e]From ref 4c. [f]The reported value for *n*-Bu was used (see text).

To address this question, a larger substrate screen was performed for the Pd-catalyzed asymmetric DcA of allyl diphenylglycinate imines **2**; both the regioisomeric ratio (rr) and enantiomeric ratio (er) were determined (Table 1). In addition to theseven *para*-substituted benzaldimines investigated in our previous report,[4d] three more electron-withdrawing R groups (trifluoromethyl (**2d**), iodo (**2e**), and chloro (**2g**)) and four electron-donating substituents (isobutyl (**2j**), *tert*-butyl (**2k**), ethyl (**2m**), and methoxy (**2n**)) were included. The substrates are arranged in descending σ^-_p values (electron-withdrawing to electron-donating) in Table 1. It should

be noted that the reported σ^-_p value for the isobutyl moiety (0.01)[10] is inexplicably and drastically different from the values of related substituents, such as isopropyl (-0.16), *tert*-butyl (-0.13), and *n*-butyl (-0.12).[6] Accordingly, the σ^-_p value for an *n*-butyl group was used in our analysis. Since the observed er values might be influenced by steric as well as electronic factors, Charton coefficients (ν),[9] which are classical steric parameters, are also provided in Table 1 for reference. An attempt was made to have a wide range of both σ^-_p and ν values so as to best extrapolate the importance of each factor. Regretfully, Charton coefficients for most strongly electron-withdrawing (nitro (**2a**), cyano (**2b**), and methyl carboxy (**2c**)) and electron-donating (methoxy, **2n**) groups are not available. In these cases, different steric parameters are available (see *Supporting Information*).[8]

A Hammett plot of the observed rr values versus σ^-_p for the asymmetric DcA of imino esters **2e-n** shows a strong ($R^2 = 0.97$) positive linear correlation, similar to our previous studies using an achiral ligand (Figure 1).[4b,d] This suggests that there is not a change in mechanism as the R groups switch from electron-withdrawing to electron-donating when the chiral ligand and DMSO are employed. This conclusion is strengthened with the expanded Hammett plot of er values versus σ^-_p (Figure 2). There is more substantial off-diagonal scatter ($R^2 = 0.79$) in this plot, but the positive linear relationship is still evident throughout the series of substrates. The higher-than-expected er value previously observed for methyl-substituted **4l** is now balanced out by the four newly included electron-rich products **4j** (*i*-Bu), **4k** (*t*-Bu), **4m** (Et), and **4n** (MeO). The observed er value for methyl-substituted **4l** is noticeably higher than the corresponding ethyl- and *tert*-butyl-substituted products (**4m** and **4k**, respectively), despite relatively similar σ^-_p values for the associated R groups (average $\Delta\sigma^-_p = 0.03$). This difference could be a result of steric factors in which the methyl substituent is just the right size (ν = 0.52) for optimal interactions with the chiral ligand upon approaching the π-allylPd(II) electrophile. Conversely, the *tert*-butyl group (**4k**) appears to be "too big" (ν = 1.24), resulting in a significant decrease in observed enantioselectivity versus expectation based on consideration of electronic factors alone. Overall, using the data in Table 1 it is possible to construct a predictive linear free energy relationship between the electronic and steric factors in the *para*-substituted benzaldimines **2** and the enantiomeric ratios of the corresponding products **4** in the asymmetric Pd-catalyzed DcA using (*S,S*)-*f*-binaphane as a chiral ligand; efforts toward this end are detailed in the *Supporting Information*.

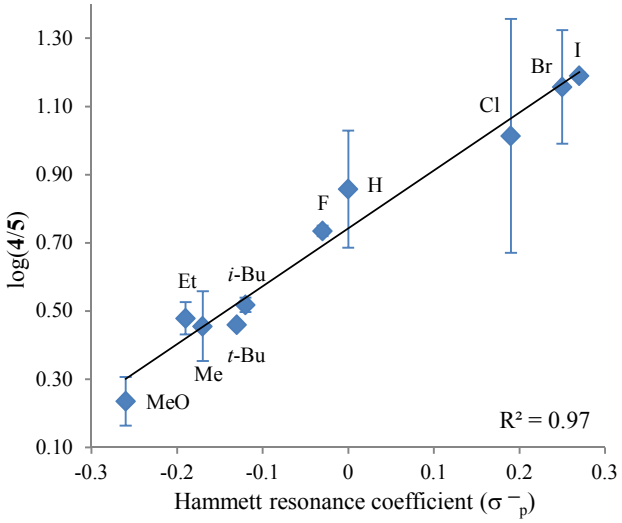


Figure 1. Hammett plot of the regioselectivity of the Pd-catalyzed asymmetric DcA of imino ester **2e-n** [log(**4**/**5**)] versus the corresponding Hammett resonance coefficients for *para* substituents (σ^-_p);[6] see Table 1, entries 5-14. Log(**4**/**5**) values were determined from ^{1}H-NMR analysis and are an average of three runs; error bars are ± standard deviation (corrected with Student's T test). The reported R^2 value was determine by standard linear regression line fitting.

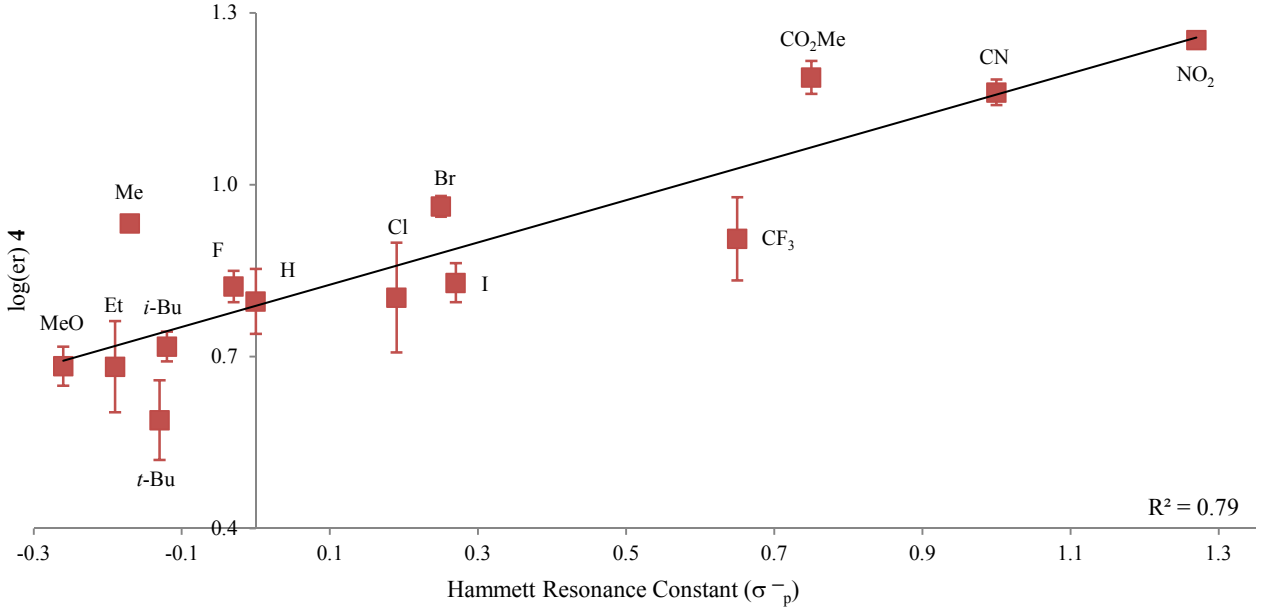
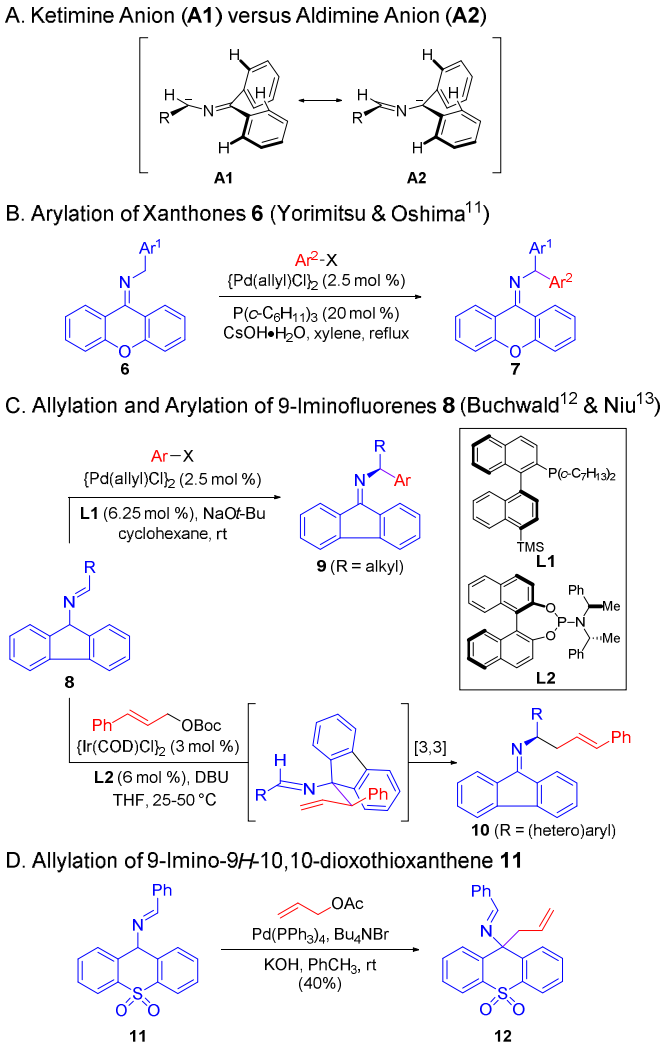


Figure 2. Hammett plot of the enantioselectivity of the Pd-catalyzed asymmetric DcA of imino esters **2a-n** [log(*S*/*R*)] versus the corresponding Hammett resonance coefficients for *para* substituents (σ^-_p);[6] see Table 1. Log(er) **4** values determined from chiral HPLC analysis and are an average of three runs; error bars are ± standard deviation (uncorrected). The reported R^2 value was determine by standard linear regression line fitting.

The formation of regioisomers **4** and **5** in the Pd-catalyzed DcA of allyl diphenylglycinate imines **2** arises from the allylation of either 2-azaallyl anion resonance isomers **A1** or **A2**, respectively (Scheme 2A). As evidenced by the results in Table 1 and Figure 1, the electronic nature of the R group greatly influences this regioselectivity, with electron-donating R groups increasing the relative amount of allylation at the more sterically hindered diphenylmethine position in **A2**. Alternatively, changing the steric and electronic elements in the 2,2-diarylglycine amino acid linchpin should also impact this regioselectivity. For example, Yorimitsu and Oshima observed that switching to xanthone imines **6** from the corresponding benzophenone imines resulted in significantly improved arylation at the less hindered position to afford diarylmethylimines **7** in the Pd-catalyzed arylation of 2-azaallyl anions (Scheme 2B).[11] The situation is more complex for fluorenone-based systems (Scheme 2C). Buchwald reported that the Pd-catalyzed asymmetric arylation of fluorenone-based 2-azaallyl anions of alkyl imines **8** (R = alkyl) proceeds with exlcusive regioselective arylation at the less substituted position to afford fluorenone imines **9**.[12] Niu and co-workers, on the other hand, determined that asymmetric allylation of 2-azaallyl anions derived from (hetero)aryl imines **8** (R = (hetero)aryl) under Ir-catalysis initially occurred at the more substituted position followed by rapid [3,3]-sigmatropic rearrangement under the reaction conditions to afford homoallylic imines **10** in high yield and enantiomeric excess.[13] Similarly, in previously unpublished studies, we determined that the Pd-catalyzed allylation of the 2-azaallyl anion derived from deprotonation of 10,10-dioxothioxanthene **11** proceeded exclusively at the more substituted carbon to afford benzaldimine **12** in modest yield (Scheme 2D).

Scheme 2. Regioselectivity in the Transition Metal-Mediated Alkylation/Arylation of 2-Azaallyl Anions



Scheme 2. Regioselectivity in the Transition Metal-Mediated Alkylation/Arylation of 2-Azaallyl Anions

A. Ketimine Anion (**A1**) versus Aldimine Anion (**A2**)

B. Arylation of Xanthones **6** (Yorimitsu & Oshima[11])

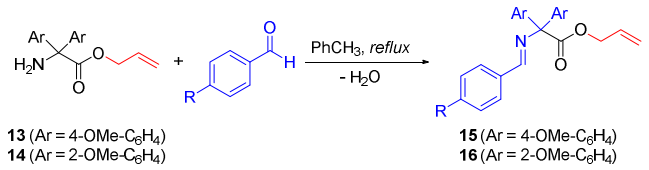
C. Allylation and Arylation of 9-Iminofluorenes **8** (Buchwald[12] & Niu[13])

D. Allylation of 9-Imino-9*H*-10,10-dioxothioxanthene **11**

In regard to the regioselectivity observed for the Pd-catalyzed DcA of allyl 2,2-diarylglycinate imines like **2**, changing the steric and electronic factors in the amino acid linchpin should also have a profound impact. To explore this hypothesis, we first synthesized the allyl esters of 2,2-di(4-methoxyphenyl)glycine (**13**) and 2,2-di(2-methoxyphenyl)glycine (**14**) following a modification of procedures recently reported by Bertus and co-workers (*see Supporting Information*)[14] and then condensed these amines with a series of *para*-substituted benzaldehydes to afford a collection of imines **15** and **16**, respectively (Scheme 3). The *para* substituent (R group) in these benzaldimines was varied to span the range of highly electron-withdrawing (R = CN) to electron-donating (R = OMe). Imino esters **15** and **16** were next subjected to our previously reported racemic Pd-catalyzed DcA reaction conditions and the resulting regioisomeric ratios (rr) were compared to the rr values obtained with the analogous 2,2-diphenylglycinate imino esters **2** (Table 2). Throughout the whole series of 2,2-di(4-methoxyphenyl)glycinates **15** (entries 2, 5, 8, 11, & 14), the resulting rr values (**17**:**18**) were consistently higher than those obtained from 2,2-diphenylglycinates **2** (**4**:**5**, entries 1, 4, 7, 10, and 13), without a substantial drop in isolated yield. As expected, the electron-donating character of the *para*-methoxy substituents in the amino acid linchpin of **15** pushes electron density away from the more substituted carbon in the 2-azaallyl anion intermediate (i.e., **A2** → **A1**, Scheme 2A), thus providing stronger preference for the desired homoallylic imine products **17** over the regioisomers **18**. This is most pronounced for the 4-methoxybenzaldimine **15n**, in which there is an 86% increase in the rr versus that seen for analogous imine **2n** (4.1:1 vs 2.2:1, respectively).

Moving the methoxy groups to the *ortho* positions in the 2,2-diarylglycine linchpin should introduce a new steric drive for allylation at the less substituted position of the corresponding 2-azaallyl anions, in addition to the electronic push provided by the electron-donating nature of the methoxy groups. In accord with this hypothesis, all of the allyl 2,2-di(2-methoxyphenyl)glycinate

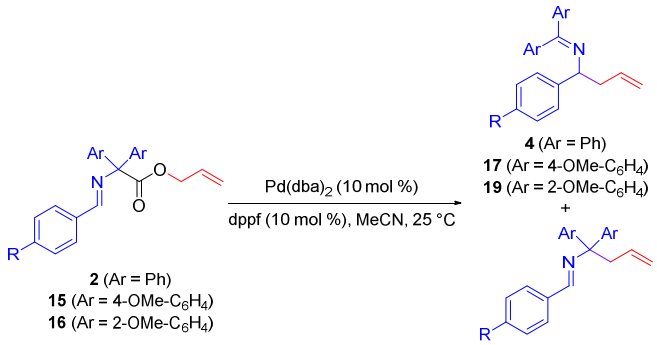
Scheme 3. Synthesis of New Allyl 2,2-Diarylglycinate Imines



13 (Ar = 4-OMe-C_6H_4)
14 (Ar = 2-OMe-C_6H_4)

15 (Ar = 4-OMe-C_6H_4)
16 (Ar = 2-OMe-C_6H_4)

Table 2. Effect of the 2,2-Diarylglycine Linchpin on the Regioselectivity of the Pd-Catalyzed DcA



2 (Ar = Ph)
15 (Ar = 4-OMe-C_6H_4)
16 (Ar = 2-OMe-C_6H_4)

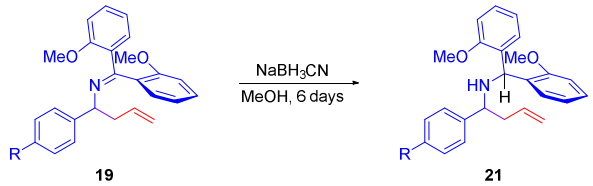
4 (Ar = Ph)
17 (Ar = 4-OMe-C_6H_4)
19 (Ar = 2-OMe-C_6H_4)
+
5 (Ar = Ph)
18 (Ar = 4-OMe-C_6H_4)
20 (Ar = 2-OMe-C_6H_4)

entry	R	σ_p^- [a]	Ar[b]	Yield[c]	rr[d]
1	CN	1.00	Ph (**2b**)	91%[e]	>20:1[e]
2			PMP (**15b**)	96%	>20:1
3			OMP (**16b**)	>98%	>20:1[f]
4	H	0.00	Ph (**2h**)	96%[e]	6.1:1.0[e]
5			PMP (**15h**)	84%	10.1:1.0
6			OMP (**16h**)	89%	>20:1[f]
7	F	-0.03	Ph (**2i**)	97%[e]	5.5:1.0[e]
8			PMP (**15i**)	79%	6.3:1.0
9			OMP (**16i**)	>98%	>20:1[f]
10	Me	-0.17	Ph (**2l**)	80%[e]	3.1:1[e]
11			PMP (**15l**)	80%	5.7:1.0
12			OMP (**16l**)	88%	>20:1[e]
13	MeO	-0.26	Ph (**2n**)	52%	2.2:1
14			PMP (**15n**)	74%	4.1:1
15			OMP (**16n**)	93%	>20:1[f]

[a]Hammett resonance coefficient for *para* substituent (ref 6). [b]PMP = 4-OMe-C_6H_4, OMP = 2-OMe-C_6H_4. [c]Average isolated combined yield over three runs. [d]Determined by ^{1}H NMR analysis of the crude reaction mixture; average of three runs and is written in **4**:**5** (Ar = Ph), **17**:**18** (Ar = (4-MeO)Ph), or **19**:**20** (Ar = (2-MeO)Ph). [e]From ref 4b. [f]Regioisomeric ratio (*rr*) determined by ^{1}H NMR analysis after reduction of the imine to the corresponding amine **21** with $NaBH_3CN$ (Scheme 4).

It should be noted that, due to hindered rotation about the aryl-C(imine) bonds in the di(2-methoxyphenyl)ketimines **19** and the imines (**16**) tested in the racemic Pd-catalyzed DcA transformation (Table 2, entries 3, 6, 9, 12, & 15) exclusively afforded the desired homoallylic imines **19** as the sole regioisomeric products. resultant broadening in the ^{1}H NMR spectra, ^{1}H NMR analysis of the crude reaction mixtures for the Pd-catalyzed DcA of imines **16** could not be used to determine the rr values of **19** versus **20**. Instead, the filtered crude reaction mixtures were first treated with $NaBH_3CN$ in MeOH to reduce the imine groups and the resultant amines **21** were then analyzed by ^{1}H NMR spectroscopy to determine the rr values (Scheme 4). In all cases, only the diphenylmethylamine products **21** were observed without any trace of the corresponding regioisomeric product arising from benzaldimines **20**. In short, switching to the 2,2-di(2-methoxy-phenyl)glycine linchpin (i.e. **2** → **16**) completely solved the regioselectivity issue for the corresponding Pd-catalyzed DcA reactions. Moreover, in all but one case (**2h** versus **16h**), the Pd-catalyzed DcA of imines **16** proceeded in notably higher isolated yields versus the corresponding 2,2-diphenylglycinates **2**. This is most pronounced when comparing the *p*-methoxybenzaldimines **16n** and **2n** (Table 2, entries 15 and 13, respectively), in which the former exclusively provides the corresponding homoallylic imine **19n** in 93% isolated yield, whereas the latter generates homoallylic imine **4n** as a 2.2:1 mixture with regioisomer **5n** in 52% combined isolated yield.

Scheme 4. Reduction of Imines 19 to Amines 21

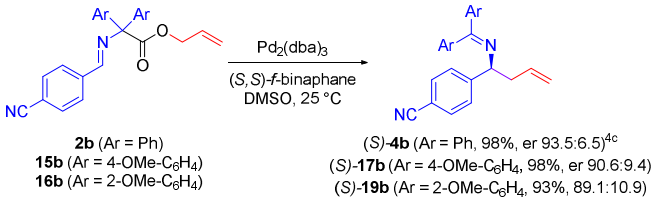


19 **21**

Having determined that addition of methoxy groups at either the *para* or *ortho* positions of the amino acid linchpin improves the regioselectivity of the Pd-catalyzed DcA of allyl 2,2-diarylglycinate imines, the influence of these electron-donating substituents on the er for the corresponding asymmetric transformations using (*S,S*)-*f*-binaphane as a chiral ligand was next explored. Initial comparisons focused on the *p*-cyanobenzaldimines **2b**, **15b**, and **16b** (Scheme 5). In our previous report, **2b** proved to be one of the best substrates for the asymmetric Pd-catalyzed DcA reaction, affording (*S*)-**4b** in essentially quantitative isolated yield with an er of 93.5:6.5.[4c] This er value could be improved to at least 98:2 (and 88% isolated yield) by selective crystallization of the racemate of **4b** from hexanes and concentration of the resultant mother liquor. Following otherwise identical reaction conditions (2.5 mol % $Pd_2(dba)_3$, 5 mol % (*S,S*)-*f*-binaphane, 0.1 M in DMSO, 25 °C), imino esters **15b** and **16b** converted to the corresponding homoallylic imines **17b** and **19b** in equally high isolated yield (98% and 93%, respectively). The resultant er values, however, were lower than that observed for benzophenone imine **4b**. The di(4-methoxyphenyl)ketimine **17b** was obtained with an average er value of 90.6:9.4, whereas the more sterically congested di(2-methoxyphenyl)ketimine **19b** was isolated with an even lower average er (89.1:10.9) in comparison to the parent compound benzophenone imine **4b**. This modest reduction in er is not surprising. As outlined above (Table 1 & Figure 2), addition of electron-donating groups into the π-network of the 2-azaallyl anion

intermediate generally results in decreased enantioselectivity. Accordingly, while introduction of the electron-donating methoxy groups into the 2,2-diarylglycine linchpin framework has a positive impact on regioselectivity, it also has a slightly negative impact on enantioselectivity.

Scheme 5. Effect of Diarylaglycine Linchpin on Enantioselectivity for the Pd-Catalyzed Asymmetric DcA of *p*-Cyanobenzaldimines

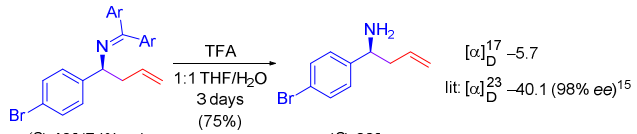


2b (Ar = Ph)
15b (Ar = 4-OMe-C_6H_4)
16b (Ar = 2-OMe-C_6H_4)

(*S*)-**4b** (Ar = Ph, 98%, er 93.5:6.5)[4c]
(*S*)-**17b** (Ar = 4-OMe-C_6H_4, 98%, er 90.6:9.4)
(*S*)-**19b** (Ar = 2-OMe-C_6H_4, 93%, 89.1:10.9)

We next explored the generality of the relationship between the nature of the 2,2-diarylglycine linchpin and the resultant er value for the asymmetric DcA transformation. Unfortunately, all chiral di(4-methoxyphenyl)ketimines **17**, with the exception of benzonitrile **17b**, proved to be prohibitively challenging to separate into individual enantiomers by chiral-phase analytical HPLC. This phenomenon, in combination with the superior regioselectivities observed for the Pd-catalyzed DcA of allyl 2,2-di(2-methoxyphenyl)glycinate imines **16**, inspired us to focus exclusively on the asymmetric synthesis of di(2-methoxyphenyl)ketimines **19**, as summarized in Table 3. In most cases, the homoallylic imines **19** were obtained with lower er values (5-11% decrease) in comparison to the corresponding benzophenone imines **4** (compare with Table 1, entries 2, 6, 8, 9, 12, & 14). One remarkable exception is with *p*-methoxybenzaldimine **16n**, which converted exclusively to **19n** in 71% isolated yield and an average *er* of 87.6:12.4 (Table 3, entry 6). The analogous 2,2-diphenylglycinate **2n** transformed under otherwise identical reaction conditions to a 1.7:1 mixture of chiral benzophenone imine **4n** (*er* 82.7:17.3) and aldimine **5n** in 68% combined yield (Table 1, entry 14). The enantiopurity of all imines **19** could be improved substantially by selective removal of the racemates by crystallization from hexanes. The configuration of *p*-bromo-substituted **19f** was confirmed to be (*S*) by hydrolysis of the imine and comparison of the optical rotation value of the resultant amine **22f** with literature reports (Scheme 6);[15] the configurations of the other products **19** were assumed to also be (*S*) by analogy.

Scheme 6. Hydrolysis of Imine (*S*)-19f



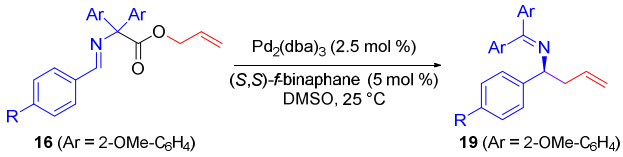
(*S*)-**19f** (74% *ee*)
(Ar = 2-OMe-C_6H_4)

(*S*)-**22f**

$[\alpha]_D^{17}$ –5.7
lit: $[\alpha]_D^{23}$ –40.1 (98% *ee*)[15]

As a final exploration of the generality of using methoxylated 2,2-diarylglycines as amino acid linchpins in the synthesis of homoallylic amines via Pd-catalyzed DcA reactions, we condensed 2-bromopiperonal and 2-furanaldehyde with allyl 2,2-di(4-methoxyphenyl)glycine (**13**) and allyl 2,2-di(2-methoxyphenyl)-glycine (**14**) to afford the corresponding imines **15o**, **15p**, **16o**,

Table 3. Pd-Catalyzed Asymmetric DcA of Allyl 2,2-Di(2-methoxyphenyl)glycinate Benzaldimines.

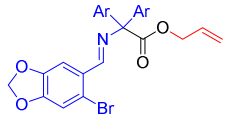


16 (Ar = 2-OMe-C_6H_4)

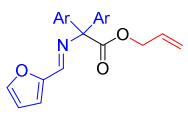
19 (Ar = 2-OMe-C_6H_4)

entry	R	σ_p^{-a}	Product	Yield[b]	er[c]
1	CN	1.00	**19b**	93% (61%)[d]	89.1:10.9 (98.7:1.3)[e]
2	Br	0.25	**19f**	85% (64%)[d]	86.8:13.2 (90.4:9.6)[e]
3	H	0.00	**19h**	87% (38%)[d]	83.2:17.1 (88.3:11.7)[e]
4	F	-0.03	**19i**	84% (44%)[d]	77.5:22.5 (86.3:13.7)[e]
5	Me	-0.17	**19l**	81% (43%)[d]	80.9:19.1 (84.5:15.5)[e]
6	MeO	-0.26	**19n**	71% (66%)[d]	87.6:12.4 (92.5:7.5)[e]

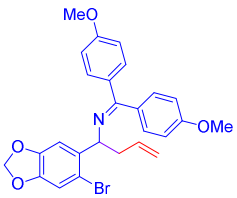
[a]Hammett resonance coefficient for *para* substituent (ref. 6). [b]Average isolated yield over three runs. [c]Determined by chiral-phase HPLC analysis; average of three runs. [d]Isolated yield after recrystallization from hexane. [e]Er of concentrated mother liquor after recrystallizing out the racemate from hexanes.



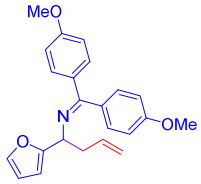
15o (Ar = 4-OMe-C_6H_4)
16o (Ar = 2-OMe-C_6H_4)



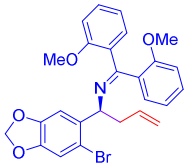
15p (Ar = 4-OMe-C_6H_4)
16p (Ar = 2-OMe-C_6H_4)



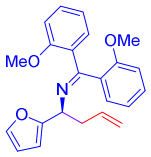
(±)-**17o**
(50%)



(±)-**17p**
(68%, 6.8:1 with **18p**)



(*S*)-**19o**
(83%, *er* 87.6:12.4)



(*S*)-**19p**
(83%, *er* 71.5:28.5)

Figure 3. Other substrates and products

and **16p** (Figure 3). Subjection of *o*-bromo-substituted aldimine **15o** to our racemic reaction conditions (10 mol % $Pd(dba)_2$, 10 mol % dppf, MeCN, 25 °C)[4b] afforded racemic **17o** exclusively (without any of the potential regioisomer **18o**) in moderate isolated yield (50%). When 2-furanyl imine **15p** was subjected to theracemic reaction conditions, however, **17p** was generated as a 6.8:1 mixture with the aldimine regioisomer **18p** in 68% com-

bined yield. Exposure of 2,2-di(2-methoxyphenyl)glycinate **16o** to our asymmetric reaction conditions (2.5 mol % $Pd_2(dba)_3$, 5 mol % (*S,S*)-*f*-binaphane, DMSO, 25 °C)[4c] generated homoallylic imine (*S*)-**19o** in 83% isolated yield and moderate er (87.6:12.4). The corresponding 2-furanyl imine **16p** afforded (*S*)-**19p** exclusively in identical isolated yield (83%) but reduced enantiopurity (*er* 71.5:28.5). These results further highlight that 2,2-di(2-methoxyphenyl)glycine is a superior amino acid linchpin in regards to regioselectivity, but further optimization of the reaction conditions (most likely in the nature of the chiral ligand) is still required to afford a truly general method for the Pd-catalyzed asymmetric DcA of allyl 2,2-diarylglycinate imines.

In summary, we have explored the electronic and steric factors (within the imine component and the amino acid linchpin) governing the regioselectivity and enantioselectivity of the Pd-catalyzed asymmetric DcA of allyl 2,2-diarylglycinate imines using (*S,S*)-*f*-binaphane as a chiral ligand. These expanded studies strongly reaffirm the positive linear Hammett correlations between the electronic nature of the *para*-substituted benzaldimine component in the substrate and the regioselectivity and enantioselectivity of the transformation. The results indicate that a change in reaction mechanism does not occur as the imines become more electron-rich. More importantly, our efforts identified 2,2-di(2-methoxyphenyl)glycine as a superior amino acid linchpin for the transformations with regards to isolated yield and regioselectivity. The *o*-methoxy groups provide both an electronic push and a steric influence that lead to exclusive allylation of the less substituted carbon of the 2-azaallyl anion intermediate, regardless of other factors. This combination of steric and electronic driving forces can be applied immediately as a general strategy for the highly regioselective functionalization of 2-azaallyl anion imine umpolungs;[1,2] further studies toward this end are currently in progress.

EXPERIMENTAL SECTION

General Methods. All non-aqueous reactions were performed in oven-dried flasks or vials under an atmosphere of dried and deoxygenated argon with dry solvents and magnetic stirring, unless stated otherwise. All solvents were dried by storing over activate 3Å molecular sieves for at least 48 h and sparged with dried and deoxygenated argon gas for at least 30 min.[16] *O*-Allyl 2,2-diphenylglycinate was synthesized according to reported procedures.[4b-c,7] Allyl esters **13** and **14** were synthesized following a modification of procedures reported by Bertus and co-workers.[15] Imino esters **2f**, **2h**, **2i**, **2l**, and **2n** were generated following reported procedures.[4b,c] Benzaldehyde was filtered through basic alumina and distilled under reduced pressure immediately prior to use. Allyl bromide was filtered through a pipette of basic alumina immediately prior to use. All other reagents were purchased from commercial sources and used as received. All chromatography was performed with indicated solvents and 60Å 230-400 mesh silica gel. Unless otherwise noted, all yields in the main text refer to average isolated yields after column chromatography of at least two separate runs at different scales. Accordingly, these yields may differ from the specific examples provided below. Enantiomeric ratios (er) were determined from samples separated on a Chiral Technologies Diacel OD-H chiral column (PDA/UV detection) and compared to a racemic standard; elution protocol for homoallylic imines **4f**, **4h**, **4i**, and **4l** matched reported procedures.[4c] Melting points are uncorrected. Infrared spectra were obtained using a thin film deposited on freshly made KBr disks; only strong and functional group-specific peaks are reported (in cm^{-1}). Optical rotation was determined in a 10 cm length polarimeter cell; all $[\alpha]_D$ values are given in 10^{-1} $degcm^2g^{-1}$ at the indicated temperature; concentrations listed in mg/mL. All NMR spectra were taken on a 400 MHz spectrometer at 300 K, as indicated. Chemical shifts are reported in δ (ppm) units using residual solvent peak as a standard.[17] Initial regioisomeric ratios (rr) determined from ^{1}H NMR analysis of the crude reaction mixtures. High resolution mass spectra obtained using an LCMS-IT-TOF.

General Procedures for the Condensation of Allyl 2,2-Diarylglycinate Imines 2, 15, and 16.[4b-c,7] To a flame-dried round bottom flask equipped with a magnetic stir bar and a Dean-Starke trap was added the appropriate allyl 2,2-diarylglycinate (1.00 equiv) and the requisite aldehyde (0.95-0.98 equiv) in toluene (0.2 M). The reaction mixture was heated to reflux (130 - 150 °C) and stirred at that temperature until completion, as determined by TLC. Concentration in vacuo and purification by flash chromatography with the indicated eluent afforded the corresponding imines **2**, **15**, or **16**, respectively.

General Procedures for the Racemic Pd-Catalyzed DcA of Allyl 2,2-Diphenylglycinate Imines 2, 15, and 16 [Procedure A].[4b] To a flame-dried screw-cap (with septum) vial equipped with a magnetic spin vane was added imine **2**, **15**, or **16** (1 equiv), dppf (10 mol %), and $Pd(dba)_2$ (10 mol %). The vial was deoxygenated with three vacuum/Ar-fill cycles and the solids were then dissolved in dry MeCN (0.1 M). The resulting reaction mixture was stirred at 25 °C for 24 h and then passed through a short plug of silica gel using the indicated eluent to remove catalyst and ligand. The regioisomeric ratio (rr) was determined by ^{1}H NMR analysis of the resulting concentrated crude reaction mixture. For characterization purposes of new compounds, an analytical sample of homoallylic imines **4** or **17** were obtained by several purifications via flash chromatography. Due to hindered rotation about the 2-MeOPh-C(imine) bond in imines **19**, peak resolution in most ^{1}H NMR were not suitable for determining *rr* values. Accordingly, imines **19** were reduced to the corresponding amines **21** prior to analysis (*see below*).

General Procedures for the Asymmetric Pd-Catalyzed DcA of Allyl 2,2-Diphenylglycinate Imines 2, 15, and 16 [Procedure B].[4c] To a flame-dried screw-cap (with septum) vial equipped with a magnetic spin vane was added imine **2**, **15**, or **16** (1 equiv), $Pd_2(dba)_3$ (2.5 mol %), and (*S,S*)-*f*-binaphane (5 mol %).[5] The vial was deoxygenated with three vacuum/Ar-fill cycles and the solids were then dissolved in dry DMSO (0.1 M). The resulting reaction mixture was stirred at 25 °C for 24 h and then passed through a short plug of silica gel using the indicated eluent to remove catalyst and ligand. The regioisomeric ratio (rr) was determined by ^{1}H NMR analysis of the resulting concentrated crude reaction mixture. The resulting enantiomeric (and frequently regioisomeric) mixtures for **4**, **17**, and **19** were then analyzed by chiral HPLC and compared to racemic samples using the indicated eluents and flow rates to determine the corresponding er values.

*Allyl (E)-2-((4-(trifluoromethyl)benzylidene)amino)-2,2-diphenyl-2-acetate (**2d**).* Imine **2d** was synthesized by condensation

between allyl 2,2-diphenylglycinate and 4-(trifluoromethyl)-benzaldehyde and was purified by flash chromatography (1% Et_3N in 2% EtOAc/hexanes) to afford a yellow solid (0.30 g, 0.71 mmol, 78%): R_f = 0.19 (1% Et_3N in 2% EtOAc/hexanes); mp 74.4 - 75.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.3 Hz, 3H), 7.67 (d, J = 8.2 Hz, 2H), 7.45 – 7.29 (m, 10H), 5.85 (ddt, J = 17.1, 10.7, 5.4 Hz, 1H), 5.16 (dtt, J = 10.5, 2.6, 1.4 Hz, 2H), 4.70 (dt, J = 5.4, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 162.1, 142.2, 131.6, 129.4, 129.1, 128.2, 127.9, 125.7 (q, J_{C-F} = 3.9 Hz), 118.5, 79.8, 66.4; IR (thin film) ν 3099, 2901, 2346, 1747, 1647, 1318; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{21}F_3NO_2^+$ 424.1519; Found 424.1547; *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{20}F_3NNaO_2^+$ 446.1338; Found 446.1319.

*Allyl (E)-2-((4-iodobenzylidene)amino)-2,2-diphenylacetate (**2e**).* Imine **2e** was synthesized by condensation between allyl 2,2-diphenylglycinate and 4-iodobenzaldehyde and was purified by flash chromatography (1% Et_3N in 2% EtOAc/hexanes) to afford a white solid (0.59 g, 1.23 mmol, 92%): R_f = 0.31 (1% Et_3N in 2% EtOAc/hexanes); mp 71.2 − 73.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.79 – 7.74 (m, 2H), 7.57 – 7.52 (m, 2H), 7.40 – 7.28 (m, 10H), 5.85 (ddt, J = 17.1, 10.7, 5.4 Hz, 1H), 5.17 (dq, J = 9.4, 1.4 Hz, 1H), 5.14 (dq, J = 2.7, 1.4 Hz, 1H), 4.69 (dt, J = 5.4, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 162.5, 142.3, 137.9, 135.9, 131.6, 130.3, 129.4, 128.2, 127.8, 118.4, 98.1, 79.6, 66.4; IR (thin film) ν 3443, 1733, 1644, 1218, 1196; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}INO_2^+$ 482.0611; Found 482.0616; *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{20}INNaO_2^+$ 504.0431; Found 504.0389 .

*Allyl (E)-2-((4-chlorobenzylidene)amino)-2,2-diphenylacetate (**2g**).* Imine **2g** was synthesized by condensation between allyl 2,2-diphenylglycinate and 4-chlorobenzaldehyde and purified by flash chromatography (1% Et_3N in 3% EtOAc/hexanes) to afford a yellow oil (0.42 g, 1.08 mmol, 87%): R_f = 0.45 (1% Et_3N in 3% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.79 – 7.75 (m, 2H), 7.42 – 7.29 (m, 12H), 5.85 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.18 (dq, J = 9.5, 1.4 Hz, 1H), 5.14 (dq, J = 2.7, 1.4 Hz, 1H), 4.70 (dt, J = 5.4, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 162.1, 142.3, 137.2, 135.0, 131.6, 130.0, 129.4, 129.0, 128.2, 127.8, 118.4, 79.6, 66.4; IR (thin film) ν 3441, 2923, 1734, 1644, 1217, 1198; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}ClNNaO_2^+$ 390.1255; Found 390.1265; *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{20}ClNNaO_2^+$ 412.1041; Found 412.1041.

*Allyl (E)-2-((4-isobutylbenzylidene)amino)-2,2-diphenylacetate (**2j**).* Imine **2j** was synthesized by condensation between allyl 2,2-diphenylglycinate and 4-isobutylbenzaldehyde and was purified by flash chromatography (1% Et_3N in 2% EtOAc/hexanes) to afford a yellow oil (0.51 g, 1.24 mmol, 98%): R_f = 0.44 (1% Et_3N in 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.41 (ddd, J = 5.7, 3.9, 2.2 Hz, 4H), 7.39 – 7.27 (m, 6H), 7.20 (d, J = 8.1 Hz, 2H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.17 (dq, J = 26.2, 1.5 Hz, 1H), 5.16 (dt, J = 3.0, 1.4 Hz, 1H), 4.71 (dt, J = 5.4, 1.5 Hz, 2H), 2.51 (d, J = 7.2 Hz, 2H), 1.88 (dp, J = 13.6, 6.8 Hz, 1H), 0.91 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 163.4, 145.4, 142.7, 134.2, 131.7, 129.5, 129.4, 128.7, 128.1, 127.6, 118.4, 79.5, 66.3, 45.5, 30.4, 22.5; IR (thin film) ν 3024, 2955, 1736, 1642, 1218, 1198; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; Found 412.2271; *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{29}NNaO_2^+$ 434.2091; Found 434.2033

*Allyl (E)-2-((4-(tert-butyl)benzylidene)amino)-2,2-diphenylacetate (**2k**).* Imine **2k** was synthesized by condensation between allyl 2,2-diphenylglycinate and 4-(*tert*-butyl)benzaldehyde and was purified by flash chromatography (1% Et_3N in 2% EtOAc/hexanes) to afford a yellow solid (0.49 g, 1.19 mmol, 86%): R_f = 0.21 (1% Et_3N in 2% EtOAc/hexanes); mp 157.3 - 158.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.81 – 7.73 (m, 2H), 7.49 – 7.27 (m, 12H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.17 (tq, J = 10.4, 1.5 Hz, 2H), 4.70 (dt, J = 5.4, 1.5 Hz, 2H), 1.34 (d, J = 2.9 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 163.2, 154.7, 142.7, 134.0, 131.8, 129.4, 128.7, 128.1, 127.6, 125.7, 118.4, 79.5, 66.3, 35.1, 31.4; IR (thin film) ν 3475, 3046, 2957, 2366, 1734, 1632 1201; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_2^+$ 412.2271; Found 412.2274; *m/z*: $[M+Na]^+$ Calcd for $C_{28}H_{29}NNaO_2^+$ 434.2091; Found 434.2048.

*Allyl (E)-2-((4-ethylbenzylidene)amino)-2,2-diphenylacetate (**2m**).* Imine **2m** was synthesized by condensation between allyl 2,2-diphenylglycinate and 4-ethylbenzaldehyde and was purified by flash chromatography (1% Et_3N in 2% EtOAc/hexanes) to afford a yellow oil (0.42 g, 1.10 mmol, 75%): R_f = 0.28 (1% Et_3N in 2% EtOAc/hexanes);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.47 – 7.17 (m, 13H), 5.95 – 5.77 (m, 1H), 5.25 – 5.09 (m, 2H), 4.70 (dd, J = 4.0, 1.4 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 1.25 (dd, J = 7.9, 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 163.3, 147.9, 142.7, 134.3, 131.7, 129.4, 128.9, 128.2, 128.1, 127.6, 118.3, 79.5, 66.3, 29.1, 15.6; IR (thin film) ν 2369, 1729, 1643, 1448, 1208; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{26}NO_2^+$ 384.1958; Found 384.1956; *m/z:* $[M+Na]^+$ Calcd for $C_{26}H_{25}NNaO_2^+$ 406.1778; Found 406.1727.

*N-(Diphenylmethylene)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-amine (**4d**).* Enantioenriched (*S*)-**4d** was synthesized from **2d** (95.3 mg, 0.25 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent: 1% Et_3N in 1% EtOAc/hexanes) to afford imino ester **4d** as a yellow oil (67.6 mg, 0.18 mmol, 79%; average er 88.9:11.1). An analytical sample of pure **4c** was obtained by repetitive flash chromatography: R_f = 0.31 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.8}_D$ -33.1 (*c* 9.1 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (m, 2H), 7.64 – 7.53 (m, 2H), 7.52 – 7.31 (m, 8H), 7.13 – 7.02 (m, 2H), 5.67 (ddt, J = 17.6, 10.4, 7.1 Hz, 1H), 5.07 – 4.95 (m, 2H), 4.52 (dd, J = 7.6, 5.6 Hz, 1H), 2.71 (dt, J = 14.0, 7.5 Hz, 1H), 2.60 (ddd, J = 13.7, 6.8, 5.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 148.7, 140.0, 137.1, 135.3, 130.4, 128.9, 128.7, 128.7, 128.3, 128.0, 127.7, 125.4 (q, J_{C-F} = 3.8 Hz), 117.5, 66.4, 44.1; IR (thin film) ν 3086, 2915, 2330,1618, 1447,1347; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{21}F_3N^+$ 380.1621; Found 380.1609; Chrial HPLC conditions: eluent: 100% hexanes, flow rate: 0.5 mL/min, average (*S*)-**4d** retention time = 12.18 min, average (*R*)-**4d** retention time = 13.82 min.

*N-(1-(4-Iodophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (**4e**).* Enantioenriched (*S*)-**4e** was synthesized from **2e** (104.3 mg, 0.22 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent: 1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil (average 15.5:1 mixture with aldimine regioisomer **5e**, 74.5 mg, 0.17 mmol, 77% combined yield; average er 87.1:12.9). An analytical

sample of pure **4e** was obtained by repetitive flash chromatography: R_f = 0.31 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.0}_D$ -29.3 (*c* 0.067, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.57 (m, 4H), 7.47 – 7.39 (m, 3H), 7.39 – 7.30 (m, 3H), 7.11 – 7.00 (m, 4H), 5.63 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.03 – 4.91 (m, 2H), 4.38 (dd, *J* = 7.6, 5.6 Hz, 1H), 2.64 (dt, *J* = 14.9, 7.5 Hz, 1H), 2.58 – 2.48 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 144.2, 139.8, 137.4, 137.0, 135.3, 130.0, 129.2, 128.6, 128.4, 128.0, 127.8, 117.0, 92.0, 66.0, 43.8; IR (thin film) ν 3059 2926, 1624, 1482, 1446; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}IN^+$ 438.0713; Found 438.0711; *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{20}INNaO_2^+$ 504.0431; Found 504.0389; Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4e** retention time = 5.49 min, average (*R*)-**4e** retention time = 6.02 min.

N-(1-(4-Chlorophenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4g). Enantioenriched (*S*)-**4g** was synthesized from **2g** (86.3 mg, 0.22 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent: 1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil (average 10.5 : 1 mixture with aldimine regioisomer **5g**, 70.0 mg, 0.20 mmol, 91% combined yield, average er 86.3:13.7). An analytical sample of pure **4g** was obtained by repetitive flash chromatography: R_f = 0.58 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.8}_D$ −21.7 (*c* 3.4 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H), 7.44 (tt, *J* = 3.9, 1.8 Hz, 3H), 7.41 – 7.31 (m, 3H), 7.30 – 7.23 (m, 4H), 7.05 (ddd, *J* = 7.2, 5.0, 3.4 Hz, 2H), 5.64 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.02 – 4.97 (m, 1H), 4.97 – 4.94 (m, 1H), 4.42 (dd, *J* = 7.7, 5.6 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.60 s– 2.51 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 143.1, 140.0, 137.1, 135.4, 132.4, 130.2, 130.2, 128.7, 128.6, 128.5, 128.5, 128.2, 128.1, 127.9, 117.2, 65.9, 44.0; IR (thin film) ν 3436, 3060, 2928, 1624, 1490; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{21}ClN^+$ 346.1357; Found 346.1340; Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4g** retention time = 5.21 min, average (*R*)-**4g** retention time = 5.78 min.

N-(1-(4-Isobutylphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4j). Enantioenriched (*S*)-**4j** was synthesized from **2j** (87.6 mg, 0.21 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent:1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil (average 3.3:1 mixture with aldimine regioisomer **5j**, 75.0 mg, .0.20 mmol, >98% combined yield; average er 83.9:16.1). An analytical sample of pure **4j** was obtained by repetitive flash chromatography: R_f = 0.65 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.7}_D$ -9.1 (*c* 6.1 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.43 – 7.38 (m, 3H), 7.35 – 7.27 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.10 – 7.03 (m, 4H), 5.64 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 4.97 (ddd, *J* = 27.8, 2.2, 1.2 Hz, 1H), 4.95 (t, *J* = 2.5 Hz, 1H), 4.40 (dd, *J* = 8.0, 5.4 Hz, 1H), 2.68 (dt, *J* = 14.1, 7.6 Hz, 1H), 2.61 – 2.52 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.84 (dp, *J* = 13.6, 6.8 Hz, 1H), 0.89 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 141.8, 140.3, 140.2, 137.3, 136.1, 129.9, 129.1, 128.7, 128.4, 128.3, 128.1, 126.9, 116.7, 66.4, 45.3, 44.1, 30.4, 22.6, 22.6; IR (thin film) ν 3058, 2955, 2924, 1622, 1442; HRMS (ESI+) *m/z*: $[M+H]^+$Calcd for $C_{27}H_{30}N^+$ 368.2373; Found 368.2357; Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4j** retention time = 4.33 min, average (*R*)-**4j** retention time = 4.71 min.

N-(1-(4-Tert-butylphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4k). Enantioenriched (*S*)-**4k** was synthesized from **2k** (74.5 mg, 0.20 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent:1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil (average 3.3:1 mixture with aldimine regioisomer **5k**, 75.0 mg, 0.20 mmol, 88% combined yield; average er 79.7:20.3). An analytical sample of pure **4k** was obtained by repetitive flash chromatography: R_f = 0.25 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.8}_D$ -13.4 (*c* 2.8 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.43 (ddd, *J* = 10.1, 4.6, 2.0 Hz, 3H), 7.37 – 7.28 (m, 5H), 7.27 – 7.22 (m, 2H), 7.12 – 7.06 (m, 2H), 5.64 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.04 – 4.91 (m, 2H), 4.41 (dd, *J* = 8.1, 5.3 Hz, 1H), 2.69 (dt, *J* = 15.3, 7.8 Hz, 1H), 2.57 (ddd, *J* = 13.6, 6.6, 5.5 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 149.6, 141.5, 137.3, 136.1, 129.9, 128.7, 128.7, 128.4, 128.4, 128.2, 128.1, 126.9, 125.3, 116.7, 66.3, 43.9, 34.6, 31.7; IR (thin film) ν 3072, 2986, 2374, 1605, 1463,1277; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{30}N^+$ 368.2373; Found 368.2358; Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4k** retention time = 4.33 min, average (*R*)-**4k** retention time = 4.61 min.

N-(1-(4-Tolyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4l). Racemic **4l** synthesized from **2l** following the general procedures mentioned above [Procedure B]. Passed through a small plug of silica gel to afford a mixture of ketimine **4l** and aldimine **5l** (average 2.9:1 mixture with aldimine regioisomer **5l**, 81% combined yield). Characterization data matched reported values for enantiomerically enriched **4l**.[4c]

N-(Diphenylmethylene)-1-(4-ethylphenyl)but-3-en-1-amine (4m). Enantioenriched (*S*)-**4m** was synthesized from **2m** (63.3 mg, 0.17 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent: 1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil (average 3.3:1 mixture with aldimine regioisomer **5m**, 48.8 mg, .0.14 mmol, 87% combined yield; average er 82.7:17.3). An analytical sample of pure **4m** was obtained by repetitive flash chromatography: R_f = 0.22 (1% Et_3N in 1% EtOAc/hexanes); $[\alpha]^{16.8}_D$ -11.8 (*c* 3.3 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.43 (ddd, *J* = 10.1, 4.6, 2.0 Hz, 3H), 7.37 – 7.28 (m, 5H), 7.27 – 7.22 (m, 2H), 7.12 – 7.06 (m, 2H), 5.64 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.04 – 4.91 (m, 2H), 4.41 (dd, *J* = 8.1, 5.3 Hz, 1H), 2.69 (dt, *J* = 15.3, 7.8 Hz, 1H), 2.57 (ddd, *J* = 13.6, 6.6, 5.5 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 149.6, 141.5, 137.3, 136.1, 129.9, 128.7, 128.7, 128.4, 128.4, 128.2, 128.1, 126.9, 125.3, 116.7, 66.3, 43.9, 34.6, 31.6; IR (thin film) ν 3044, 2901, 2345, 1647, 1463,1292; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}N^+$ 340.2060; Found 340.2037; Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4m** retention time = 4.48min, average (*R*)-**4m** retention time = 5.01 min.

N-(1-(4-Methoxyphenyl)but-3-en-1-yl)-1,1-diphenylmethanimine (4n) Enantioenriched (*S*)-**4n** was synthesized from **2n** (91.1 mg, 0.20 mmol) following the general procedures described above [Procedure B]. Passed through a small plug of silica gel (eluent:1% Et_3N in 1% EtOAc/hexanes) to afford a yellow oil

(average 1.7 : 1 mixture with aldimine regioisomer **5n**, 55.8 mg, 016 mmol, 69% combined yield; average er 82.7:17.3). An analytical sample of pure **4n** was obtained by repetitive flash chromatography: R_f = 0.21 (1% Et_3N in 1% EtOAc/hexanes); ^1H NMR and ^{13}C NMR spectra matched literature reports for the racemic material:[4b] $[\alpha]^{16.3}_D$ -10.1 (*c* 9.02 x 10^{-3}, EtOAc); Chiral HPLC conditions: eluent: 0.2:99.8 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**4n** retention time = 6.70 min, average (*R*)-**4n** retention time = 8.22 min.

9-(Benzylideneamino)-9H-thioxanthene 10,10-dioxide (***11***). To a stirred solution of 9*H*-thioxanthen-9-one 10.10-dioxide (1.0 g, 4.1 mmol) and benzylamine (2.02 mL, 18.5 mmol) in toluene (15 mL) at 0 °C was added dropwise via addition funnel a solution of $TiCl_4$ (0.34 mL, 3.1 mmol) in toluene (5 mL). The resulting mixture was stirred at rt for 30 min, then heated to reflux and stirred at that temperature overnight. After cooling to rt, the mixture was filtered through Celite, concentrated in vacuo, and crystalized from Et_2O to afford benzaldimine **11** as a white powder (772 mg, 2.3 mmol, 56%): R_f = 0.46 (20% EtOAc/hexanes); mp 289.9 - 290.3 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.14 (tt, *J* = 4.9, 2.5 Hz, 2H), 8.08 - 8.01 (m, 2H), 7.62 - 7.46 (m, 9H), 5.93 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 141.6, 136.5, 135.3, 132.5, 132.2, 129.2, 129.1, 127.9, 126.2, 124.1, 66.6; IR (thin film) ν 3457, 2930, 2346, 1647, 1643, 1292, 1292, 1163; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{16}NO_2S^+$ 334.0896; Found 334.0892; *m/z*: $[M+Na]^+$ Calcd for $C_{20}H_{16}NNaO_2S^+$ 356.0716; Found 356.0682.

9-Allyl-9-(benzylideneamino)-9H-thioxanthane 10,10-dioxide (***12***). To a slurry of benzaldimine **11** (30 mg, 0.09 mmol), tetrabutylammonium bromide (2.9 mg, 9.0 μmol), $Pd(PPh_3)_4$ (10.4 mg, 9.0 μmol), and KOH (10 mg, 0.18 mmol) in toluene (1 mL) at rt was added in one portion via syringe allyl acetate (0.02 mL, 0.23 mmol) and the resulting mixture was stirred vigorously at rt for 5 h then concentrated in vacuo. The resulting residue was purified by flash chromatography (5% → 10% EtOAc/hexanes) to afford the allylated product **12** as an off-white solid (13 mg, 0.04 mmol, 40%): R_f = 0.40 (10% EtOAc/hexanes); mp 236.7 - 237.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.31 – 8.12 (m, 2H), 8.01 – 7.77 (m, 2H), 7.67 – 7.45 (m, 6H), 7.44 – 7.33 (m, 2H), 5.63 (ddt, *J* = 17.3, 10.3, 7.1 Hz, 1H), 4.95 (dd, *J* = 23.2, 6.0 Hz, 2H), 3.32 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 142.9, 136.3, 132.9, 132.5, 132.0, 129.1, 129.0, 128.8, 128.3, 123.7, 119.6, 66.7, 47.9; IR (thin film) ν 3457, 3086, 2902, 2359, 1618, 1292, 1149; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{20}NO_2S^+$ 374.1209; Found 374.1220; *m/z*: $[M+Na]^+$ Calcd for $C_{23}H_{19}NNaO_2S^+$ 396.1029; Found 396.1001.

Allyl 2-amino-2,2-bis(4-methoxyphenyl)acetate (***13***). To a solution of *tert*-butyl (2-hydroxy-1,1-bis(4-methoxyphenyl)ethyl)-carbamate (0.52 g, 1.39 mmol)[14] in DMSO (10 mL. 0.2 M) was added in one portion IBX (0.47 g, 1.68 mmol, 1.2 equiv) and the reaction was stirred at 25 °C for 3 h. The resulting mixture was then diluted with sat. aq $NaHCO_3$ (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 20% EtOAc/hexanes) to afford *tert*-butyl(1,1-bis(4-methoxyphenyl)-2-oxoethyl)carbmate as a yellow oil (0.45 g, 1.21 mmol, 87%): R_f = 0.46 (20% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 9.52 (s, 1H), 7.33 – 7.20 (m, 4H), 6.96 – 6.87 (m, 4H), 6.07 (s, 1H), 3.82 (s, 6H), 1.51 – 1.04 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 159.4, 154.0, 132.3, 129.8, 128.9, 113.9, 113.5, 80.0, 70.7, 55.3, 53.5, 28.2; IR (thin film) ν 3404, 2719, 1717, 1254, 1179; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{25}NNaO_5^+$ 394.1625; Found 394.1610.

To a solution of the resulting aldehyde (5.05 g, 13.6 mmol) in 1:1 MeCN/H_2O (140 mL, 0.2 M) were added successively NaH_2PO_4 (3.26 g, 27.2 mmol, 2.0 equiv), H_2O_2 (30 w/v %, 0.95 g, 2 equiv), and $NaClO_2$ (1.94 g, 21.4 mmol, 1.5 equiv). The resulting reaction mixture was stirred at 25 °C until complete as determined by TLC. Solid Na_2SO_3 then was added to the mixture, which was then stirred at rt for 3 h. The resulting quenched reaction was diluted with sat. aq $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 10% MeOH/CH_2Cl_2) to afford 2((*tert*-butoxycarbonyl)amino)-2,2-bis(4-methoxyphenyl)acetate) as a white solid (4.49 g, 11.6 mmol, 85%): R_f = 0.29 (10% MeOH/CH_2Cl_2). NMR spectra matched published reports.[14]

To a slurry of the resulting carboxylic acid (3.16 g, 8.15 mmol) in EtOH (40 mL, 0.2M) was added KOH (0.51 g, 9.10 mmol, 1.1 equiv) and the mixture was stirred at 25 °C. After complete dissolution of solids, the solvent was removed by rotary evaporation. The resulting yellow oil was dissolved in DMF (40 mL, 0.2M) and to the resulting solution was added dropwise via addition funnel allyl bromide (0.75 mL, 8.66 mmol, 1.1 equiv). After stirring at 25 °C overnight, the reaction mixture was diluted with a combination of DI H_2O (20 mL) and brine (20 mL) and extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with 10 w/v % aq LiCl (2 × 15 mL) to remove any residual DMF, then dried (Na_2SO_4), filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 10% EtOAc/hexanes) to afford allyl 2-((*tert*-butoxycarbonyl)amino)-2,2-bis(4-methoxyphenyl)acetate as a yellow oil (3.35 g, 7.85 mmol, 96%): R_f = 0.67 (20% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 4H), 6.84 (d, *J* = 8.9 Hz, 4H), 6.06 (s, 1H), 5.83 (ddd, *J* = 22.7, 10.9, 5.6 Hz, 1H), 5.24 – 5.13 (m, 2H), 4.66 (d, *J* = 5.6 Hz, 2H), 3.78 (s, 6H), 1.57 – 1.11 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 158.9, 154.1, 132.4, 131.4, 129.5, 118.7, 113.5, 113.2, 79.9, 68.5, 66.7, 55.2, 28.3; IR (thin film) ν 3430, 1723, 1648, 1253, 1180; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{29}NNaO_6^+$ 450.1887; Found 450.1882.

Finally, the resulting allyl ester (2.95 g, 6.90 mmol) was dissolved in 1 M HCl in EtOAc (prepared by bubbling dry HCl gas into dry EtOAc then diluting to 1 M with additional EtOAc, 5 equiv of HCl) and the resulting reaction mixture was stirred at 25 °C until complete disappearance of starting material, as determined by TLC. The resulting mixture then was diluted with sat. aq $NaHCO_3$ (80 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with brine, dried ($MgSOs_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 20% EtOAc/hexanes) to afford amine **13** as a yellow oil (2.24 g, 6.85 mmol, >98%): R_f = 0.44 (20% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27

(m, 4H), 6.89 – 6.81 (m, 4H), 5.93 – 5.79 (m, 1H), 5.24 – 5.14 (m, 2H), 4.67 (ddd, J = 8.4, 4.9, 1.4 Hz, 2H), 3.80 (s, 6H), 2.21 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 158.9, 136.1, 131.6, 129.5, 128.8, 118.6, 113.4, 67.5, 66.3, 55.3; IR (thin film) ν 3387, 3318, 1729, 1647; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{21}NNaO_4^+$ 350.1363; Found 350.1356.

*Allyl 2-amino-2,2-bis(2-methoxyphenyl)acetate (**14**).* To a stirred solution of cyanomethyl 1-naphthoate (6.02 g, 28.5 mmol)[14] in THF (140 mL) at 0 °C was added dropwise via addition funnel a solution of (2-methoxy)phenylmagnesium bromide (32 mL, 2M in THF, 2.2 equiv). The resulting reaction mixture was stirred at 0 °C for 30 min, then 1M aq HCl (50 mL) and EtOAc (50 mL) were added successively. The resulting aqueous later was extracted with more EtOAc (2 × 50 mL) and the combined organic layers were wash with brine, dried ($MgSO_4$), filtered, and concentration in vacuo. The resulting residue was purified by flash chromatography (eluent: 30% EtOAc/hexanes) to afford *N*-(2-hydroxy-1,1-bis(2-methoxyphenyl)ethyl-1-naphthamide as a white solid (4.21 g, 9.85 mmol, 35%): R_f = 0.31 (30% EtOAc/hexanes); mp 140.1 − 141.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.38 (m, 1H), 7.98 (br s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.69 (d, J = 7.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.50 – 7.43 (m, 1H), 7.38 (d, J = 7.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.02 – 6.90 (m, 4H), 5.49 (dd, J = 8.1, 4.8 Hz, 1H), 4.79 (d, J = 6.9 Hz, 2H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 157.2, 135.5, 134.0, 130.8, 130.4, 130.2, 129.2, 129.1, 128.4, 127.2, 126.6, 125.8, 125.0, 124.9, 120.9, 112.6, 69.4, 66.0, 55.7; IR (thin film) ν 3392, 3361, 3307, 1645; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{26}NO_4^+$ 428.1856; Found 428.1860; $[M+Na]^+$ Calcd for $C_{27}H_{25}NNaO_4^+$ 450.1676; Found 450.1634.

A solution of the resulting naphthamide (4.21 g, 9.85 mmol) and NaOH (1.14 g, 28.5 mmol, 3.0 equiv) in EtOH (50 mL, 0.2 M) was stirred at 135 °C for 2 h in a high pressure glass reaction bottle. After cooling to rt, $(Boc)_2O$ (6.8 mL, 29.6 mmol, 3 equiv) was added and the resulting solution was stirred at 40 °C for 7 d. The resulting reaction mixture was partitioned between H_2O (50 mL) and Et_2O (50 mL). The aqueous phase was extracted with more Et_2O (2 × 50 mL) and the combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 15% EtOAc/hexanes) to afford *tert*-butyl-(2-hydroxy-1,1-bis(2-methoxyphenyl)ethyl)carbamate as a yellow solid (2.34 g, 6.27 mmol, 64%): R_f = 0.33 (15% EtOAc/hexanes); mp 108.5 − 109.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.6 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.91 (dd, J = 11.2, 4.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 4.71 (br s, 1H), 4.61 (d, J = 6.6 Hz, 2H), 3.50 (s, 6H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 156.1, 131.4, 128.4, 120.5, 112.6, 79.5, 66.5, 65.0, 55.6, 28.4; IR (thin film) ν 3569, 3405, 1711, 1250, 1158; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{27}NNaO_5^+$ 396.1781; Found 396.1767.

To a solution of the resulting alcohol (2.34 g, 6.27 mmol) in DMSO (20 mL, 0.2M) was added in one portion IBX (2.11 g, 7.54 mmol, 1.2 equiv) and the reaction was stirred at rt for 3 d. The resulting reaction mixture was then diluted with sat. aq $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude residue was purified by flash chromatography (eluent: 10% EtOAc/hexane) to afford *tert*-butyl(1,1-bis(2-methoxyphenyl)-2-oxoethyl)carbamate as a white solid (1.96 g, 5.28 mmol, 84%): R_f = 0.28 (10% EtOAc/hexane); mp 90.6 − 92.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of rotational isomers) 9.82 (s, 1H), 7.35 – 7.26 (m, 2H), 7.22 (d, J = 7.6 Hz, 2H), 7.01 – 6.92 (m, 2H), 6.90 (d, J = 8.1 Hz, 2H), 6.42 (br s, 1H), 3.66 (s, 6H), 1.41 – 1.04 (br m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (mixture of rotational isomers) 195.2, 158.4, 156.3, 132.7, 130.8, 130.5, 129.6, 125.6, 120.8, 120.4, 111.5, 79.2, 69.7, 55.8, 55.5, 28.3, 27.7; IR (thin film) ν 3409, 1716, 1244, 1165; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{25}NNaO_5^+$ 394.1625; Found 394.1616.

To a solution of the resulting aldehyde (1.09 g, 2.93 mmol) in 1:1 $MeCN/H_2O$ (20 mL, 0.2M) were added successively NaH_2PO_4 (0.70 g, 5.83 mmol, 2.0 equiv), H_2O_2 (30 w/v %, 0.68 g, 2 equiv), and $NaClO_2$ (0.49 g, 5.41 mmol, 1.5 equiv). The resulting reaction mixture was stirred at 25 °C until complete as determined by TLC. Solid Na_2SO_3 then was added to the mixture, which was then stirred at 25 °C for 4 d. The resulting quenched reaction was diluted with sat. aq $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 10% $MeOH/CH_2Cl_2$) to afford 2-((*tert*-butoxycarbonyl)amino)-2,2-bis(2-methoxyphenyl)acetic acid as a white solid (0.91 g, 2.35 mmol, 80%): R_f = 0.29 (30% EtOAc/hexane); mp 62.7 − 64.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.13 (br s, 2H), 7.00 – 6.96 (m, 2H), 6.93 (t, J = 7.5 Hz, 2H), 6.43 (br s, 1H), 3.76 (s, 6H), 1.35 (br s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 156.7, 130.5, 130.1, 125.3, 120.8, 112.3, 80.7, 60.4, 55.9, 28.3; IR (thin film) ν 3419, 2969, 1733, 1249, 1165; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{25}NNaO_6^+$ 410.1574; Found 410.1567.

To a vigorously stirred slurry of the resulting carboxylic acid (2.67 g, 6.89 mmol) in EtOH (35 mL, 0.2M) was added KOH (0.46 g, 8.21 mmol, 1 equiv). After complete dissolution of solids, the solvent was removed by rotary evaporation and the resultant yellow oil was redissolved in DMF (35 mL, 0.2M). To this stirred solution was added dropwise via addition funnel allyl bromide (1.02g, 8.43 mmol, 1 equiv). After stirring at 25 °C overnight, the reaction mixture was diluted with a combination of DI H_2O (15 mL) and brine (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with 10 w/v % aq LiCl (2 × 10 mL) to remove any residual DMF, dried (Na_2SO_4), filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 20% EtOAc/hexanes) to afford the corresponding allyl ester as a white solid (2.77 g, 6.49 mmol, 94%): R_f = 0.64 (20% EtOAc/hexanes); mp 111.6 − 112.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.7 Hz, 4H), 6.96 – 6.81 (m, 4H), 6.40 (s, 1H), 5.86 (ddt, J = 16.1, 10.7, 5.5 Hz, 1H), 5.13 (dq, J = 11.8, 1.3 Hz, 2H), 4.66 (d, J = 5.2 Hz, 2H), 3.62 (s, 6H), 1.65 – 1.00 (m, 9H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 171.1, 157.3, 154.2, 132.0, 130.3, 129.0, 127.7, 120.0, 117.9, 112.0, 79.1, 67.4, 66.2, 60.4, 55.7, 28.3 ; IR (thin film) ν 3443, 3072, 2972, 1723, 1253, 1160; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{29}NNaO_6^+$ 450.1887; Found 450.1875.

Finally, the resulting allyl ester (2.77 g, 6.49 mmol) was dissolved in 1 M HCl in EtOAc (prepared by bubbling dry HCl gas into dry EtOAc then diluting to 1 M with additional EtOAc, 5 equiv of HCl) and the resulting reaction mixture was stirred at 25 °C until complete disappearance of starting material, as determined by TLC. The resulting mixture then was diluted with sat. aq $NaHCO_3$ (80 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. The resulting residue was purified by flash chromatography (eluent: 5% MeOH/CH_2Cl_2) to afford amine **14** as a pale yellow solid (2.01 g, 6.14 mmol, 95%): R_f = 0.56 (10% MeOH/CH_2Cl_2); mp 64.5 − 66.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (tt, J = 9.9, 2.1 Hz, 2H), 7.09 (dd, J = 7.8, 1.7 Hz, 2H), 6.95 (dd, J = 8.2, 0.9 Hz, 2H), 6.89 (td, J = 7.6, 1.1 Hz, 2H), 5.96 – 5.81 (m, 1H), 5.16 (dq, J = 6.1, 1.5 Hz, 1H), 5.12 (t, J = 1.4 Hz, 1H), 4.66 (dt, J = 5.6, 1.4 Hz, 2H), 3.78 (s, 6H), 2.60 (br s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 157.6, 132.4, 130.8, 129.1, 120.8, 117.8, 111.6, 66.4, 65.8, 55.6; IR (thin film) ν 3389, 2973, 1746, 1244; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_4^+$ 328.1543; Found 328.1527.

*Allyl (E)-2-((4-cyanobenzylidene)amino)-2,2-bis(4-methoxyphenyl)acetate (**15b**)*. Imine **15b** was synthesized by condensation between amino ester **13** and 4-formylbenzonitrile following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 13% EtOAc/hexanes) to afford a yellow solid (0.54 g, 1.23 mmol, 87%): R_f = 0.23 (1% Et_3N in 10% EtOAc/hexanes); mp 97.3−98.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.86 (s, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.31 – 7.26 (m, 4H), 6.92 – 6.85 (m, 4H), 5.85 (ddt, J = 17.1, 10.7, 5.4 Hz, 1H), 5.19 (dq, J = 10.9, 1.4 Hz, 1H), 5.15 (dq, J = 4.0, 1.4 Hz, 1H), 4.68 (dt, J = 5.4, 1.4 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 161.1, 159.1, 140.3, 134.1, 132.5, 131.6, 130.6, 129.2, 118.7, 118.5, 114.3, 113.5, 79.0, 66.4, 55.4; IR (thin film) ν 3434, 3071, 2995, 1729, 1643, 1254, 1179; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{24}N_2NaO_4^+$ 463.1628; Found 463.1623.

*Allyl (E)-2-(benzylideneamino)-2,2-bis(4-methoxyphenyl)acetate (**15h**)*. Imine **15h** was synthesized by condensation between amino ester **13** and benzaldehyde following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 5% EtOAc/hexanes) to afford a white solid (1.02 g, 2.45 mmol, 78%): R_f = 0.35 (1% Et_3N in 10% EtOAc/hexanes); mp 77.7−79.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.84 – 7.79 (m, 2H), 7.46 – 7.38 (m, 3H), 7.33 – 7.28 (m, 4H), 6.90 – 6.84 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.20 (ddd, J = 17.2, 3.1, 1.6 Hz, 1H), 5.15 (ddd, J = 10.5, 2.7, 1.3 Hz, 1H), 4.69 (dt, J = 5.4, 1.5 Hz, 1H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 162.8, 158.9, 136.6, 134.7, 131.8, 131.1, 130.6, 128.9, 128.7, 118.4, 113.4, 78.7, 66.2, 55.4; IR (thin film) ν 3000, 2937, 1728, 1646, 1254, 1224; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{25}NNaO_4^+$ 438.1676; Found 438.1661.

*Allyl (E)-2-((4-fluorobenzylidene)amino)-2,2-bis(4-methoxyphenyl)acetate (**15i**)*. Imine **15i** was synthesized by condensation between amino ester **13** and 4-fluorobenzaldehyde following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 10% EtOAc/hexanes) to afford a clear off-white oil (0.52 g, 1.20 mmol, 98%): R_f = 0.42 (1% Et_3N in 10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 3H), 7.33 – 7.27 (m, 4H), 7.14 – 7.06 (m, 2H), 6.91 – 6.84 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.22 – 5.13 (m, 2H), 4.68 (dt, J = 5.4, 1.5 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 164.7 (d, J_{C-F} = 251.1 Hz), 161.4, 159.0, 134.6, 132.9 (J_{C-F} = 3.0 Hz), 131.8, 130.8 (J_{C-F} = 8.7 Hz), 130.6, 118.4, 115.8 (J_{C-F} = 21.8 Hz), 113.4, 78.7, 66.3, 55.4; IR (thin film) ν 3440, 2934, 1732, 1644, 1252, 1178; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{26}H_{24}FNNaO_4^+$ 456.1582; Found 456.1576.

*Allyl (E)-2-((4-methylbenzylidene)amino)-2,2-bis(4-methoxyphenyl)acetate (**15l**)*. Imine **15l** was synthesized by condensation between amino ester **13** and 4-methylbenzaldehyde following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 10% EtOAc/hexanes) to afford a yellow oil (0.86 g, 2.00 mmol, 89%): R_f = 0.36 (1% Et_3N in 10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71 (d, J = 8.1 Hz, 2H), 7.33 – 7.28 (m, 4H), 7.22 (d, J = 7.9 Hz, 2H), 6.90 – 6.84 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.20 (ddd, J = 17.2, 3.1, 1.6 Hz, 1H), 5.15 (ddd, J = 10.5, 2.7, 1.3 Hz, 1H), 4.69 (dt, J = 5.4, 1.5 Hz, 2H), 3.82 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 162.6, 158.9, 141.5, 134.8, 134.0, 131.8, 130.6, 129.4, 128.8, 118.3, 113.4, 78.6, 66.2, 55.4, 21.7; IR (thin film) ν 3439, 3001, 2933, 1732, 1642, 1251, 1178; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_5^+$ 446.1962; Found 446.1965; *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{27}NNaO_5^+$ 468.1781; Found 468.1744.

*Allyl (E)-2,2-bis(4-methoxyphenyl)-2-((4-methoxybenzylidene)amino)acetate (**15n**)*. Imine **15n** was synthesized by condensation between amino ester **13** and 4-methoxybenzaldehyde following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 15% EtOAc/hexanes) to afford a yellow oil (1.31 g, 2.94 mmol, 79%): R_f = 0.38 (1% Et_3N in 15% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.78 – 7.74 (m, 2H), 7.32 – 7.27 (m, 4H), 6.95 – 6.90 (m, 2H), 6.89 – 6.84 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.19 (ddd, J = 17.5, 3.3, 1.7 Hz, 1H), 5.14 (ddd, J = 10.5, 2.8, 1.4 Hz, 1H), 4.68 (dt, J = 5.4, 1.5 Hz, 2H), 3.84 (s, 3H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 162.0, 158.9, 135.0, 131.9, 130.6, 130.5, 129.7, 118.3, 114.0, 113.4, 78.5, 66.2, 55.5, 55.4; IR (thin film) ν 3446, 3002, 1732, 1641, 1252, 1165; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_4^+$ 430.2013; Found 430.2012; *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{27}NNaO_4^+$ 452.1832; Found 452.1814.

*Allyl (E)-2-(((6-bromobenzo[d][1,3]dioxol-5-yl)methylene)amino)-2,2-bis(4-methoxyphenyl)acetate (**15o**)*. Imine **15o** was synthesized by condensation between amino ester **13** and 6-bromopiperonal following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 10% EtOAc/hexanes) to afford a clear colorless oil (0.33 g, 0.61 mmol, 53%): R_f = 0.23 (1% Et_3N in 10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.77 (s, 1H), 7.31 – 7.26 (m, 4H), 6.95 (s, 1H), 6.90 – 6.85 (m, 4H), 6.02 (s, 2H), 5.87 (ddt, J = 17.1, 10.7, 5.5 Hz, 1H), 5.24 – 5.13 (m, 2H), 4.69 (dt, J = 5.5, 1.4 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 161.6, 159.0, 150.8, 147.9, 134.5, 131.8, 130.5, 129.0, 118.5, 118.4, 113.5, 112.6, 108.2, 102.3, 78.9, 66.3, 55.4; IR (thin film) ν 3442, 2932, 1732, 1250, 1178; HRMS (ESI+) *m/z*: $[M+Na]^+$

Calcd for $C_{27}H_{24}BrNNaO_6^+$ 560.0679 & 562.0659; Found 560.0652 & 562.0643.

*Allyl (E)-2-((furan-2-ylmethylene)amino)-2,2-bis(4-methoxyphenyl)acetate (**15p**).* Imine **15p** was synthesized by condensation between amino ester **13** and 2-furanaldehyde following the general procedures described above. Purified by flash chromatography (eluent: 1% Et_3N in 15% EtOAc/hexanes) to afford a brown oil (0.33 g, 0.81 mmol, 80%): R_f = 0.13 (1% Et_3N in 10% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.56 (d, J = 1.6 Hz, 1H), 7.30 – 7.24 (m, 4H), 6.90 – 6.83 (m, 4H), 6.79 (dd, J = 3.4, 0.5 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H), 5.86 (ddt, J = 17.2, 10.7, 5.5 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.72 – 4.66 (m, 2H), 3.82 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 159.0, 152.2, 151.5, 145.3, 134.1, 131.8, 130.6, 128.9, 118.5, 115.4, 113.5, 113.4, 111.9, 78.9, 66.4, 55.4; IR (thin film) ν 2934, 1732, 1644, 1252, 1179; HRMS (ESI+) *m/z*: $[M+Na]^+$ Calcd for $C_{24}H_{23}NNaO_5^+$ 428.1468; Found 428.1449.

*Allyl (E)-2-((4-cyanobenzylidene)amino)-2,2-bis(2-methoxyphenyl)acetate (**16b**).* Imine **16b** was synthesized by condensation between amine **14** (0.52 g, 1.59 mmol) and 4-cyanobenzaldehyde (0.20 g, 1.52 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 13% EtOAc/hexanes) to afford a white solid (0.68 g, 1.54 mmol, >98%): R_f = 0.22 (1% Et_3N in 13% EtOAc/hexanes); mp 134.2 − 134.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.96 – 7.88 (m, 2H), 7.76 – 7.64 (m, 2H), 7.36 – 7.25 (m, 5H), 7.00 – 6.86 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.20 – 5.09 (m, 2H), 4.69 (dt, J = 5.4, 1.5 Hz, 2H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 159.3, 157.3, 140.7, 132.3, 132.1, 130.4, 129.3, 129.0, 128.4, 120.4, 117.7, 111.9, 77.8, 65.9, 55.4; IR (thin film) ν 3369, 2974, 1736, 1640, 1249, 1228; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{25}N_2O_4^+$ 441.1809; Found 441.1808; *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{24}N_2NaO_5^+$ 463.1628; Found 463.1610.

*Allyl (E)-2-((4-bromobenzylidene)amino)-2,2-bis(2-methoxyphenyl)acetate (**16f**).* Imine **16f** was synthesized by condensation between amine **14** (0.33 g, 1.01 mmol) and 4-bromobenzaldehyde (0.17 g, 0.91 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 20% EtOAc/hexanes) to afford a pale yellow solid (0.41 g, 0.83 mmol, 83%): R_f = 0.22 (1% Et_3N in 10% EtOAc/hexanes); mp 156.3 - 167.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.69 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.38 – 7.23 (m, 4H), 6.92 (ddd, J = 19.0, 12.8, 4.5 Hz, 4H), 5.94 – 5.78 (m, 1H), 5.23 – 5.07 (m, 2H), 4.68 (dt, J = 5.4, 1.4 Hz, 2H), 3.58 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.0, 157.4, 135.9, 132.4, 131.8, 130.6, 130.2, 129.2, 129.0, 125.2, 120.5, 117.7, 112.00, 65.9, 55.6; IR (thin film) ν 2944, 2857, 2374, 1747, 1585, 1476, 1234; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}BrNO_4^+$ 494.0967 & 496.0946; Found 494.0983 & 496.0968.

*Allyl (E)-2-(benzylideneamino)-2,2-bis(2-methoxyphenyl)acetate (**16h**).* Imine **16h** was synthesized by condensation between amine **14** (0.51 g, 1.56 mmol) and benzaldehyde (0.17 g, 1.60 mmol, 1.02 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 10% EtOAc/hexanes) to afford a white solid (0.56 g, 1.35 mmol, 87%): R_f = 0.29 (1% Et_3N in 10% EtOAc/hexanes); mp 96.6 − 97.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (td, J = 4.7, 2.9 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.35 (dd, J = 7.8, 1.7 Hz, 2H), 7.29 (dd, J = 1.7, 0.6 Hz, 1H), 7.29 (dd, J = 15.5, 1.7 Hz, 1H), 6.94 (td, J = 7.6, 1.2 Hz, 2H), 6.88 (dd, J = 8.2, 1.0 Hz, 2H), 5.87 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.16 (dq, J = 17.2, 1.6 Hz, 1H), 5.11 (ddd, J = 10.5, 2.8, 1.4 Hz, 1H), 4.68 (dt, J = 5.4, 1.5 Hz, 1H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 161.2, 157.5, 137.0, 132.5, 130.7, 130.7, 129.3, 129.1, 128.8, 128.6, 120.4, 117.6, 112.0, 65.8, 55.6; IR (thin film) ν 3465, 3065, 2995, 1774, 1639, 1248, 1191; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{26}NO_4^+$ 416.1856; Found 416.1856.

*Allyl (E)-2-((4-fluorobenzylidene)amino)-2,2-bis(2-methoxyphenyl)acetate (**16i**).* Imine **16i** was synthesized by condensation between amine **14** (0.57 g, 1.74 mmol) and 4-fluorobenzaldehyde (0.21 g, 1.69 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 10% EtOAc/hexanes) to afford a white solid (0.72 g, 1.67 mmol, >98%): R_f = 0.29 (1% Et_3N in 10% EtOAc/hexanes); mp 137.3 − 138.3 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.86 – 7.77 (m, 2H), 7.45 – 7.26 (m, 5H), 7.12 – 7.03 (m, 2H), 6.98 – 6.85 (m, 4H), 5.86 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.13 (ddq, J = 15.3, 10.5, 1.5 Hz, 2H), 4.68 (dt, J = 5.4, 1.5 Hz, 2H), 3.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 164.5 (d, $J_{C\text{-}F}$ = 250.5 Hz), 157.5, 133.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 132.4, 130.63 (d, $J_{C\text{-}F}$ = 8.6 Hz), 130.61, 129.14, 129.08, 120.4, 117.7, 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 112.0, 65.8, 55.6.; IR (thin film) ν 3442, 3080, 3054, 2996, 1731, 1633, 1251, 1224; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}FNO_4^+$ 434.1762; Found 434.1760.

*Allyl (E)-2,2-bis(2-methoxyphenyl)-2-((4-methylbenzylidene)amino)acetate (**16l**).* Imine **16l** was synthesized by condensation between amine **14** (0.92 g, 2.81 mmol) and 4-methylbenzaldehyde (0.33 g, 2.75 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 13% EtOAc/hexanes) to afford a white solid (1.09 g, 2.54 mmol, 92%): R_f = 0.33 (1% Et_3N in 13% EtOAc/hexanes); mp 141.2 − 142.8 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 5.2 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 7.37 – 7.25 (m, 5H), 7.21 (d, J = 7.9 Hz, 2H), 6.97 – 6.84 (m, 4H), 5.86 (ddt, J = 17.2, 10.6, 5.4 Hz, 1H), 5.13 (ddq, J = 21.2, 10.5, 1.5 Hz, 2H), 4.68 (dt, J = 5.4, 1.5 Hz, 2H), 3.59 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.9, 157.4, 140.9, 134.3, 132.4, 130.6, 129.2, 129.2, 128.9, 128.6, 120.3, 117.4, 111.8, 65.6, 55.5, 21.6; IR (thin film) ν 3444, 3063, 3014, 2934, 1732, 1642, 1250, 1208; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_4^+$ 430.2013; Found 430.2013.

*Allyl (E)-2-((4-methoxybenzylidene)amino)-2,2-bis(2-methoxyphenyl)acetate (**16n**).* Imine **16n** was synthesized by condensation between amine **14** (0.43 g, 1.31 mmol) and 4-methoxybenzaldehyde (0.18 g, 1.30 mmol, 0.98 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 13% EtOAc/hexanes) to afford a white solid (0.51 g, 1.15 mmol, 88%): R_f = 0.22 (1% Et_3N in 13% EtOAc/hexanes); mp 93.4 − 94.4 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 5.2 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.36 (dd, J = 7.8, 1.7 Hz, 2H), 7.31 – 7.25 (m, 3H), 6.97 – 6.84 (m, 6H), 5.93 – 5.79 (m, 1H), 5.21 – 5.05 (m, 2H), 4.67 (ddd, J = 7.2, 4.4, 2.9 Hz, 2H), 3.84 (s, 3H), 3.58 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 161.7, 160.3, 157.4, 132.4, 130.6, 130.2, 129.4, 128.8, 120.2, 117.4, 113.8, 111.9, 65.6, 55.5, 55.4; IR (thin film) ν 3069, 2998, 1732, 1631, 1245, 1162; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_5^+$ 446.1962; Found 446.1961.

*Allyl (E)-2-(((6-bromobenzo[d][1,3]dioxol-5-yl)methylene)-amino)-2,2-bis(2-methoxyphenyl)acetate (**16o**).* Imine **16o** was synthesized by condensation between amine **14** (0.46 g, 1.41 mmol) and 6-bromopiperonal (0.31 g, 1.35 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 15% EtOAc/hexanes) to afford a white solid (0.59 g, 1.09 mmol, 81%): R_f = 0.24 (1% Et_3N in 15% EtOAc/hexanes); mp 126.7 − 128.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 5.2 Hz, 1H), 7.71 (s, 1H), 7.33 – 7.28 (m, 2H), 7.21 (dd, J = 7.8, 1.6 Hz, 2H), 7.00 – 6.86 (m, 5H), 6.00 (s, 2H), 5.95 – 5.82 (m, 1H), 5.14 (ddq, J = 13.3, 10.5, 1.5 Hz, 2H), 4.70 (dt, J = 5.5, 1.4 Hz, 2H), 3.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 159.9, 157.4, 150.4, 147.7, 132.3, 130.4, 129.4, 129.1, 128.6, 120.4, 117.8, 117.7, 112.4, 111.7, 108.4, 102.1, 77.8, 65.8, 55.4; IR (thin film) ν 3441, 3076, 2962, 1727, 1621, 1246, 1167; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{25}BrNO_6^+$ 538.0860 & 540.0840; Found 538.0861 & 540.0841.

*Allyl (E)-2-((furan-2-ylmethylene)amino)-2,2-bis(2-methoxyphenyl)acetate (**16p**).* Imine **16p** was synthesized by condensation between amine **14** (0.46 g, 1.40 mmol) and 2-furanaldehyde (0.13 g, 1.35 mmol, 0.95 equiv) as described above. Purified by flash chromatography (eluent: 1% Et_3N in 20% EtOAc/hexanes) to afford a pale yellow solid (0.53 g, 1.31 mmol, 97%): R_f = 0.30 (1% Et_3N in 20% EtOAc/hexanes); mp 135.2 − 136.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.34 – 7.20 (m, 3H), 6.91 (ddt, J = 9.1, 8.2, 2.6 Hz, 2H), 6.82 – 6.74 (m, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H), 5.93 – 5.79 (m, 1H), 5.21 – 5.07 (m, 1H), 4.68 (tt, J = 6.5, 2.1 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 157.4, 152.4, 149.9, 144.8, 132.3, 130.7, 129.1, 128.5, 120.4, 117.6, 114.5, 111.9, 111.6, 77.7, 65.8, 55.4; IR (thin film) ν 3406，3103，2999，1712，1647，1249，1219; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_5^+$ 406.1649; Found 406.1647.

*4-(1-((Bis(4-methoxyphenyl)methylene)amino)but-3-en-1-yl)-benzonitrile (**17b**).* Racemic **17b** was synthesized from imino ester **15b** (99.3 mg, 0.23 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a clear colorless oil (83.6 mg, 0.21 mmol, 91%). Enantioenriched (*S*)-**17b** was synthesized from **15b** following the general procedures described above [Procedure B] to afford a yellow oil (average er 90.6 : 9.4, >98% yield): R_f = 0.33 (10% EtOAc/hexanes); $[\alpha]^{16.3}_D$ -37.5 (*c* 0.033, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 4H), 7.43 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.2 Hz, 4H), 6.88 – 6.81 (m, 2H), 5.67 – 5.54 (m, 1H), 4.99 – 4.91 (m, 2H), 4.48 (dd, J = 7.5, 5.7 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 2.61 (dt, J = 13.8, 7.4 Hz, 1H), 2.52 (ddd, J = 13.7, 6.9, 5.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 161.3, 159.5, 150.4, 134.9, 132.9, 132.2, 130.3, 129.2, 129.0, 128.0, 119.2, 117.3, 113.8, 113.4, 110.4, 65.9, 55.4, 55.3, 43.9; IR (thin film) ν 3401, 3072, 3004, 2934, 1462; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2^+$ 397.1911; Found 397.1896 . Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**17b** retention time = 22.91 min, average (*R*)-**17b** retention time = 26.37 min.

*1,1-Bis(4-methoxyphenyl)-N-(1-phenylbut-3-en-1-yl)methanimine (**17h**).* Racemic **17h** was synthesized from imino ester **15h** (64.4 mg, 0.16 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a yellow oil (average 10:1 mixture with aldimine regioisomer **18h**, 47.2 mg, 0.13 mmol, 81% combined yield). An analytical sample of pure **17h** was obtained by repetitive flash chromatography: R_f = 0.49 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.31 (dt, J = 15.0, 7.5 Hz, 4H), 7.24 – 7.18 (m, 1H), 6.96 (dd, J = 22.2, 8.8 Hz, 4H), 6.88 – 6.81 (m, 2H), 5.65 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 4.96 (t, J = 13.8 Hz, 2H), 4.45 (dd, J = 7.7, 5.6 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.75 – 2.62 (m, 1H), 2.61 – 2.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 159.4, 144.9, 136.0, 130.2, 129.4, 128.9, 128.3, 127.2, 126.6, 116.5, 113.6, 113.3, 66.3, 55.3, 55.3, 44.1; IR (thin film) ν 3067, 3003, 2931; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_2^+$ 372.1958; Found 372.1943.

*N-1-(4-Fluorophenyl)but-3-en-1-yl)-1,1-bis(4-methoxyphenyl)methanimine (**17i**).* Racemic **17i** was synthesized from imino ester **15i** (78.6 mg, 0.18 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a clear colorless oil (average 6.3:1 mixture with aldimine regioisomer **18i**, 43.8 mg, 0.11 mmol, 61% combined yield). An analytical sample of pure **17i** was obtained by repetitive flash chromatography: R_f = 0.23 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.7 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.00 – 6.91 (m, 6H), 6.84 (d, J = 8.9 Hz, 2H), 5.62 (ddt, J = 17.3, 10.2, 7.1 Hz, 1H), 4.95 (dd, J = 13.7, 7.2 Hz, 2H), 4.46 – 4.38 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.62 (dt, J = 14.2, 7.1 Hz, 1H), 2.57 – 2.47 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 161.7 (J_{CF} = 244.0 Hz), 161.2, 159.5, 140.7 ($J_{C\text{-}F}$ = 3.1 Hz), 135.8, 133.4, 130.3, 129.5, 129.4, 129.1 128.7 (J_{CF} = 7.8 Hz), 128.52, 116.9, 115.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.8, 113.4, 65.7, 55.5, 55.4, 44.3; IR (thin film) ν 3071, 3003, 2932, 1461; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{25}FNO_2^+$: 390.1864; Found 390.1848.

*1,1-Bis(4-methoxyphenyl)-N-(1-(p-tolyl)but-3-en-1-yl)methanimine (**17l**).* Racemic **17l** was synthesized from imino ester **15l** (91.8 mg, 0.21 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a yellow oil (average 5.7:1 mixture with aldimine regioisomer **18l**, 62.7 mg, 0.16 mmol, 76% combined yield). An analytical sample of pure **8d** was obtained by repetitive flash chromatography: R_f = 0.53 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 10.1 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.99 (t, J = 5.5 Hz, 2H), 6.94 (t, J = 5.5 Hz, 2H), 6.87 – 6.80 (m, 2H), 5.65 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 4.95 (dd, J = 20.4, 10.1 Hz, 2H), 4.42 (dd, J = 7.7, 5.6 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.72 – 2.61 (m, 1H), 2.60 – 2.49 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 161.0, 159.4, 141.9, 136.1, 133.5, 130.2, 129.4, 129.0, 127.0, 116.4, 113.6, 113.2, 66.0, 55.3, 55.3, 44.0, 21.1; IR (thin film) ν 3435, 3072, 3002, 2931, 1463; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_2^+$ 386.2115; Found 386.2103.

*1,1-Bis(4-methoxyphenyl)-N-(1-(4-methoxyphenyl)but-3-en-1-yl)methanimine (**17n**).* Racemic **17n** was synthesized from imino ester **15n** (69.7 mg, 0.16 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a yellow oil (average 4.1:1 mixture with aldimine regioisomer **18n**, 37.6 mg,

0.09 mmol, 56% combined yield). An analytical sample of pure **8e** was obtained by repetitive flash chromatography: R_f = 0.36 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.28 – 7.21 (m, 2H), 6.98 (dq, *J* = 13.5, 8.7 Hz, 4H), 6.88 – 6.80 (m, 4H), 5.65 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.01 – 4.89 (m, 2H), 4.41 (dd, *J* = 7.7, 5.6 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 2.64 (dt, *J* = 14.9, 7.5 Hz, 1H), 2.59 – 2.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 161.0, 159.4, 158.3, 137.1, 136.1, 133.5, 130.2, 129.6, 129.4, 128.1, 116.4, 113.7, 113.6, 113.3, 65.6, 55.3, 55.3, 55.2, 44.1; IR (thin film) ν 3001, 2932，2836, 1604, 1509, 1410, 1304, 1247, 1174; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_3^+$ 402.2064; Found 402.2055.

*N-(1-(6-Bromobenzo[d][1,3]dioxol-5-yl)but-3-en-1-yl)-1,1-bis(4-methoxyphenyl)methanimine (**17o**).* Racemic **17o** was synthesized from imino ester **15o** (54.5 mg, 0.10 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a yellow oil (26.6 mg, 0.05 mmol, 50%): R_f = 0.48 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.36 (s, 1H), 6.99 – 6.93 (m, 4H), 6.92 (s, 1H), 6.88 – 6.82 (m, 2H), 5.95 (dd, *J* = 6.1, 1.4 Hz, 2H), 5.67 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.00 – 4.91 (m, 2H), 4.85 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 2.54 – 2.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 161.3, 159.6, 147.5, 146.8, 137.7, 135.6, 133.4, 130.4, 129.5, 129.4, 116.8, 113.9, 113.4, 112.5, 112.3, 109.6, 101.7, 64.4, 55.5, 55.4, 43.2; IR (thin film) ν 3440, 3073, 3002, 2930, 1473; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}BrNO_4^+$ 494.0961 & 496.0941; Found 494.0949 & 496.0931.

*N-1-(Furan-2-yl)but-3-en-1-yl)-1,1-bis(4-methoxyphenyl)-methanimine (**17p**).* Racemic **17p** was synthesized from imino ester **15p** (70.7 mg, 0.17 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel (eluent: 10% EtOAc/hexanes) to afford a yellow oil (average 6.8:1 mixture with aldimine regioisomer **18p**, 39.9 mg, 0.11 mmol, 65% combined yield). An analytical sample of pure **8g** was obtained by repetitive flash chromatography: R_f = 0.29 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.38 – 7.33 (m, 1H), 7.18 – 7.11 (m, 2H), 7.01 – 6.94 (m, 2H), 6.87 – 6.77 (m, 2H), 6.34 – 6.28 (m, 1H), 6.16 (dt, *J* = 3.2, 0.7 Hz, 1H), 5.67 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.09 – 4.94 (m, 2H), 4.59 (dd, *J* = 7.3, 6.0 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.76 – 2.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 161.2, 159.5, 156.6, 141.4, 135.3, 133.2, 130.4, 129.6, 129.1, 117.0, 113.7, 113.3, 110.0, 105.4, 60.1, 55.4, 55.3, 39.9; IR (thin film) ν 3441, 3073, 3002, 1641, 1463; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_3^+$ 362.1751; Found 362.1739.

*4-(1-((Bis(2-methoxyphenyl)methyl)amino)but-3-en-1-yl)benzonitrile (**19b**)* Racemic **19b** was synthesized from imino ester **16b** (101.9 mg, 0.23 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19b** as a yellow solid (95.1 mg, 0.22 mmol, >98%). Enantioenriched (*S*)-**19b** was synthesized from **16b** following the general procedures described above [Procedure B] to afford a yellow solid (average er 89.1 : 10.9, 93%): R_f = 0.29 (10% EtOAc/hexanes); mp 134.8 – 135.7 °C; poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3400, 3070, 2991, 1625, 1490, 1463; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}N_2O_2^+$ 397.1916; Found 397.1903. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19b** retention time = 23.98 min, average (*R*)-**19b** retention time = 25.92 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21b**. Specifically, to a solution of imine **19b** (46.6 mg, 0.12 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (29.9 mg, 0.47 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6 d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) affording amine **21b** as a yellow solid (30.1 mg, 0.08 mmol, 67%): R_f = 0.29 (10% EtOAc/hexane); mp 103.7 – 104.8 °C; $[\alpha]^{16.6}_D$ +41.0 (*c* 6.3 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.30 (dt, *J* = 11.6, 5.8 Hz, 1H), 7.24 – 7.11 (m, 2H), 7.00 – 6.89 (m, 1H), 6.89 – 6.72 (m, 3H), 5.73 – 5.57 (m, 1H), 5.10 (d, *J* = 7.1 Hz, 2H), 5.05 (dd, *J* = 6.0, 1.8 Hz, 1H), 3.67 (t, *J* = 6.1 Hz, 6H), 2.76 (s, 1H), 2.46 – 2.31 (m, 2H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 156.8, 150.2, 135.0, 131.9, 131.6, 130.3, 128.9, 128.5, 128.4, 127.8, 127.7, 120.3, 119.3, 118.0, 110.8, 110.7, 110.4, 59.6, 55.2, 55.2, 53.7, 42.9; IR (thin film) ν 3327, 3056, 3003, 2962, 2227, 1640, 1493, 1460; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{27}N_2O_2^+$ 399.2073; Found 399.2063.

*N-(Bis(2-methoxyphenyl)methylene)-1-(4-bromophenyl)but-3-en-1-amine (**19f**).* Racemic **19f** was synthesized from imino ester **6f** (109.0 mg, 0.22 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19f** as a yellow solid (83.3 mg, 0.19 mmol, 86%). Enantioenriched (*S*)-**19f** was synthesized from **16f** following the general procedures described above [Procedure B] to afford a colorless oil (average er 86.8:13.2, 85%): R_f = 0.23 (10% EtOAc/hexanes); mp 145.8 – 147.1 °C; poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3072，2930, 2830，2374, 1605, 1490, 1276; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{25}BrNO_2^+$ 450.1069 & 452.1048; Found 450.1058 & 452.1.31. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate:1 mL/min, average (*S*)-**19f** retention time = 8.13 min, average (*R*)-**19f** retention time = 9.98 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21f**. Specifically, to a solution of imine **19f** (58.1 mg, 0.13 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (33.1 mg, 0.53 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4),

filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21f** as a yellow solid (28.0 mg, 0.06 mmol, 48%): R_f = 0.17 (10% EtOAc/hexanes); mp 167.8 - 168.3; $[\alpha]^{16.5}_D$ +35.1 (*c* 4.58 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 1H), 7.43 – 7.20 (m, 6H), 7.16 – 7.03 (m, 3H), 7.01 – 6.85 (m, 3H), 5.89 – 5.73 (m, 1H), 5.29 (s, 1H), 5.18 (dd, *J* = 13.5, 7.2 Hz, 2H), 3.78 (d, *J* = 5.1 Hz, 6H), 3.74 – 3.66 (m, 1H), 2.79 – 2.32 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 156.8, 144.0, 135.9, 131.9, 130.7, 129.0, 128.5, 127.8, 127.4, 127.3, 127.3, 126.5, 120.0, 120.0, 116.9, 110.6, 110.5, 59.5, 55.1, 55.0, 53.4.; IR (thin film) *ν* 3457, 2956, 1647, 1642, 1292,1116; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{27}BrNO_2^+$ 452.1225 & 454.1205; Found 452.1163 & 454.1190.

*N-(Bis(2-methoxyphenyl)methyl)-1-phenylbut-3-en-1-amine (**19h**).* Racemic **19h** was synthesized from imino ester **16h** (97.9 mg, 0.24 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19h** as a yellow solid (79.7 mg, 0.21 mmol, 91%). Enantioenriched (*S*)-**19h** was synthesized from **16h** following the general procedures described above [Procedure B] to afford a yellow solid (average er 83.2:16.8, 87%): R_f = 0.38 (10% EtOAc/hexanes); mp 87.3 - 88.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, poor peak resolution due to hindered rotation about the aryl–C(imine) bond) *δ* 7.55 (br d, *J* = 7.2 Hz, 1H), 7.34 – 7.10 (br m, 8H), 7.01 – 6.71 (br m, 4H), 5.70 (br s, 1H), 5.09 – 4.85 (br m, 2H), 4.35 (br s, 1H), 3.80 (br s, 1.5H), 3.55 (br s, 3H), 3.50 (br s, 3H), 3.30 (br s, 1.5H), 2.89 – 2.48 (br m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$, peaks doubled due to hindered rotation about the aryl–C(imine) bond) *δ* 165.1, 157.4, 155.8, 144.5, 144.1, 139.4, 136.4, 132.0, 130.3, 130.1, 129.6, 129.3, 128.7, 128.6, 128.5, 128.4, 128.1, 128.1, 127.4, 127.2, 126.4, 120.7, 120.0, 116.5, 115.9, 112.1, 111.1, 110.3, 66.9, 66.4, 55.8, 55.4, 54.8, 44.0, 43.1; IR (thin film) *ν* 3431, 3071, 3026, 3003, 1618, 1490, 1460; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{26}NO_2^+$ 372.1958; Found 372.1948. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19h** retention time = 7.68 min, average (*R*)-**17h** retention time = 9.84 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21h**. Specifically, to a solution of imine **19h** (73.9 mg, 0.19 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (53.1 mg, 0.84 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6 d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21h** as a yellow solid (38.4 mg, 0.10 mmol, 53%): R_f = 0.33 (10% EtOAc/hexanes); mp 84.9 – 85.4 °C; $[\alpha]^{20}_D$ +6.15 (*c* 0.011, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.32 – 7.15 (m, 7H), 7.10 (tt, *J* = 8.0, 4.0 Hz, 1H), 6.93 (td, *J* = 7.4, 1.0 Hz, 1H), 6.85 – 6.70 (m, 3H), 5.77 – 5.62 (m, 1H), 5.20 (s, 1H), 5.04 (ddd, *J* = 11.1, 2.4, 1.1 Hz, 2H), 3.62 (d, *J* = 4.9 Hz, 6H), 3.57 (dt, *J* = 9.8, 4.9 Hz, 1H), 2.69 – 2.33 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 157.7, 157.0, 144.3, 136.1, 132.1, 131.0, 129.2, 128.7, 128.0, 127.7, 127.6, 127.5, 126.7, 120.3, 120.2, 117.1, 110.9, 110.8, 59.8, 55.3, 55.2, 53.6, 43.1; IR (thin film) *ν* 3329, 3062, 3026, 3003, 1642, 1491, 1465; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{28}NO_2^+$ 374.2115; Found 374.2111.

*N-(Bis(2-methoxyphenyl)methyl)-1-(4-fluorophenyl)but-3-en-1-amine (**19i**)* Racemic **19i** was synthesized from imino ester **16i** (101.9 mg, 0.23 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19i** as a yellow solid (88.9 mg, 0.23 mmol, >98%). Enantioenriched **19i** was synthesized from **16i** following the general procedures described above [Procedure B] to afford a yellow solid (average er 77.5:22.5, 84%): R_f = 0.22 (10% EtOAc/hexanes); mp 88.3 – 90.4 °C; poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) *ν* 3435, 3071, 3004, 1619, 1489; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{25}FNO_2^+$ 390.1869; Found 390.1858. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19i** retention time = 7.84 min, average (*R*)-**19i** retention time = 9.45 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21i**. Specifically, to a solution of imine **19i** (43.5 mg, 0.11 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (26.0 mg, 0.42 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21i** as a white solid (26.1 mg, 0.06 mmol, 55%): R_f = 0.22 (10% EtOAc/hexanes); mp 107.2 – 108.5 °C; $[\alpha]^{16.2}_D$ +10.5 (*c* 0.013, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.37 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.30 – 7.18 (m, 4H), 7.13 (tt, *J* = 16.4, 8.2 Hz, 1H), 7.05 – 6.91 (m, 3H), 6.89 – 6.74 (m, 3H), 5.77 – 5.61 (m, 1H), 5.16 (s, 1H), 5.11 – 5.02 (m, 2H), 3.67 (d, *J* = 6.0 Hz, 6H), 3.63 – 3.55 (m, 1H), 2.61 – 2.31 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) *δ* 161.9 (d, $J_{C\text{-}F}$ = 243.6 Hz), 157.7, 157.0, 139.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 135.9, 132.0, 130.8, 129.2, 129.1 (d, $J_{C\text{-}F}$ = 7.9 Hz), 128.7, 127.73, 127.68, 120.4, 120.3, 117.4, 114.8 ($J_{C\text{-}F}$ = 21.0 Hz), 110.94, 110.87, 59.1, 55.4, 55.3, 53.7, 43.3; IR (thin film) *ν* 3340, 3064, 2996, 1639, 1489, 1461; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{27}FNO_2^+$ 392.2026; Found 392.2013.

*N-(Bis(2-methoxyphenyl)methyl)-1-(p-tolyl)but-3-en-1-amine (**19l**)* Racemic **19l** was synthesized from imino ester **16l** (101.0 mg, 0.23 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19l** as a yellow solid (84.8 mg, 0.22 mmol, 96%). Enantioenriched (*S*)-**19l** was synthesized from **16l** following the general procedures described above [Procedure B] to afford a yellow solid (average er 80.9:19.1, 91%): R_f = 0.33 (10%

EtOAc/hexanes); mp 77.9 – 78.7 °C; poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3439, 3065, 3002, 1619, 1489, 1460; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_2^+$ 386.2120; Found 386.2105. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19l** retention time = 7.94 min, average (*R*)-**19l** retention time = 9.37 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21l**. Specifically, to a solution of imine **19l** (41.3 mg, 0.12 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (25.9 mg, 0.41 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21l** as a white solid (20.2, 0.05 mmol, 42%). R_f = 0.33 (10% EtOAc/hexanes); mp 111.3 – 113.4 °C; $[\alpha]^{16.7}_D$ +17.0 (*c* 0.02, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.27 – 7.10 (m, 7H), 7.00 – 6.92 (m, 1H), 6.87 – 6.75 (m, 3H), 5.79 – 5.64 (m, 1H), 5.22 (s, 1H), 5.13 – 5.01 (m, 2H), 3.67 (d, *J* = 5.9 Hz, 6H), 3.57 (dd, *J* = 7.8, 6.0 Hz, 1H), 2.59 – 2.22 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 157.0, 141.2, 136.3, 136.1, 132.1, 130.9, 129.3, 128.7, 128.7, 127.5, 127.5, 120.2, 120.2, 117.0, 110.8, 110.7, 59.3, 55.3, 55.2, 53.7, 43.1, 21.2; IR (thin film) ν 3325, 3056, 3004, 2963, 1641, 1492, 1462; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_2^+$ 388.2277; Found 388.2263.

*N-(Bis(2-methoxyphenyl)methyl)-1-(4-methoxyphenyl)but-3-en-1-amine (**19n**).* Racemic **19n** was synthesized from imino ester **16n** (100.4 mg, 0.23 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 15% EtOAc/hexanes) to afford imine **19n** as a yellow solid (84 mg, 0.21 mmol, 93%). Enantioenriched (*S*)-**19n** was synthesized from **16n** following the general procedures described above [Procedure B] to afford a yellow solid (average er 87.6:12.4, 71%): R_f = 0.31 (15% EtOAc/hexane); mp 77.0 – 77.4 °C; poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3450, 3069, 3002, 2934, 1489, 1461; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_3^+$ 402.2069; Found 402.2051. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19n** retention time = 14.36 min, average (*R*)-**19n** retention time = 16.03 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21n**. Specifically, to a solution of imine **19n** (62.2 mg, 0.15 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (38.4 mg, 0.61 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 15% EtOAc/hexanes) afforded amine **21n** as a yellow solid (48.6 mg, 0.12 mmol, 80%): R_f = 0.31 (15% EtOAc/hexanes); mp 91.8 – 92.5 °C; $[\alpha]^{16.6}_D$ +19.6 (*c* 0.024, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.27 – 7.08 (m, 6H), 7.00 – 6.92 (m, 1H), 6.89 – 6.81 (m, 4H), 6.76 (t, *J* = 7.3 Hz, 1H), 5.78 – 5.63 (m, 1H), 5.20 (s, 1H), 5.07 (t, *J* = 13.5 Hz, 2H), 3.80 (d, *J* = 10.4 Hz, 3H), 3.73 – 3.63 (m, 6H), 3.59 – 3.51 (m, 1H), 2.70 – 2.31 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157.6, 157.0, 136.3, 136.2, 132.1, 130.9, 129.3, 128.7, 128.6, 127.5, 127.5, 120.2, 120.2, 117.0, 113.3, 110.8, 110.7, 59.0, 55.3, 55.2, 55.2, 53.7, 43.1.; IR (thin film) ν 3329, 3061, 2997, 1639, 1489, 1460; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_3^+$ 404.2226; Found 404.2212.

*N-(Bis(2-methoxyphenyl)methyl)-1-(6-bromobenzo[d][1,3]dioxol-5-yl)but-3-en-1-amine (**19o**)* Racemic **19o** was synthesized from imino ester **16o** (102.6 mg, 0.19 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19o** as a clear oil (95.3 mg, 0.19 mmol, >98%). Enantioenriched (*S*)-**19o** was synthesized from **16o** following the general procedures described above [Procedure B] to afford a colorless oil (average er 87.6:12.4, 83%): R_f = 0.11 (10% EtOAc/hexane poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3072, 2934, 1620, 1472; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{25}BrNO_4^+$ 494.0967 & 496.0946; Found 494.0961 & 496.0946. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19o** retention time = 16.32 min, average (*R*)-**19o** retention time = 47.35 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21o**. Specifically, to a solution of imine **19o** (37.8 mg, 0.07 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (14.8 mg, 0.24 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21o** as a colorless oil (23.8 mg, 0.04 mmol, 57%): R_f = 0.11 (10% EtOAc/hexanes); $[\alpha]^{16.7}_D$ -20.5 (*c* 0.018, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 1H), 7.28 – 7.09 (m, 4H), 6.99 – 6.90 (m, 2H), 6.89 – 6.73 (m, 3H), 5.96 (dd, *J* = 18.4, 1.4 Hz, 2H), 5.71 (dddd, *J* = 16.2, 10.2, 8.4, 5.8 Hz, 1H), 5.14 (s, 1H), 5.12 – 5.03 (m, 2H), 4.03 (dd, *J* = 8.6, 4.7 Hz, 1H), 2.52 – 1.80 (m, 4H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 156.9, 147.5, 146.8, 136.5, 135.6, 132.0, 130.8, 129.2, 128.5, 127.6, 127.5, 120.2, 120.2, 117.4, 114.1, 112.1, 110.7, 110.6, 108.8, 101.5, 57.7, 55.3, 55.2, 53.4, 41.9, 29.7; IR (thin film) ν 3348, 3072, 3001, 1638, 1470; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{27}BrNO_4^+$ 496.1123 & 498.1103; Found 496.1155 & 498.1077.

*N-(Bis(2-methoxyphenyl)methyl)-1-(furan-2-yl)but-3-en-1-amine (**19p**).* Racemic **19p** was synthesized from imino ester **16p** (103.9 mg, 0.26 mmol) following the general procedures described above [Procedure A]. Passed through a short plug of silica gel to remove catalyst and ligand (eluent: 10% EtOAc/hexanes) to afford imine **19p** as a yellow solid (82.1 mg, 0.23 mmol, 88%). Enantioenriched (*S*)-**19p** was synthesized from **16p** following the general procedures described above [Procedure B] to afford a colorless oil (average er 71.5:28.5, 83%): R_f = 0.17 (10% EtOAc/hexanes); mp 55.4 – 55.9 °C poor peak resolution in ^{1}H and ^{13}C NMR due to hindered rotation about the aryl–C(imine) bond (*see below*); IR (thin film) ν 3426, 3070, 2996, 1620, 1488, 1460; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_3^+$ 362.1756; Found 362.1745. Chiral HPLC conditions: eluent: 0.5:99.5 2-PrOH/hexane, flow rate: 1 mL/min, average (*S*)-**19p** retention time = 11.58 min, average (*R*)-**19p** retention time = 14.95 min.

Due to hindered rotation about aryl-imine bond, ^{1}H NMR analysis of the resulting product could not be used to determine the regioisomeric ratio. Accordingly, the imine was reduced to the corresponding amine **21p**. Specifically, to a solution of imine **19p** (36.5 mg, 0.10 mmol) in MeOH (0.5 mL) was added in one portion $NaBH_3CN$ (25.8 mg, 0.41 mmol, 4 equiv) and the resulting solution was stirred at rt under Ar for 6 d. The resulting reaction mixture then was diluted with CH_2Cl_2 and washed with 1N aq NaOH (the aqueous layer was extracted with two more portions of CH_2Cl_2). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated in vacuo. The resulting residue was passed through a short plug of silica gel to remove any unreacted starting imine (eluent: 10% EtOAc/hexanes) afforded amine **21p** as a colorless oil (19.8 mg, 0.05 mmol, 50%): R_f = 0.17 (10% EtOAc/hexanes); $[\alpha]^{16.8}_D$ +20.6 (*c* 5.4 x 10^{-3}, EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 9.2, 6.5, 2.5 Hz, 1H), 7.36 (dt, *J* = 5.6, 2.8 Hz, 1H), 7.27 – 7.09 (m, 4H), 6.97 (td, *J* = 7.4, 0.9 Hz, 1H), 6.87 – 6.75 (m, 3H), 6.31 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.13 (d, *J* = 3.0 Hz, 1H), 5.72 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.46 (s, 1H), 5.13 – 5.08 (m, 1H), 5.07 – 4.99 (m, 1H), 3.72 (t, *J* = 4.7 Hz, 5H), 3.67 (dd, *J* = 8.0, 5.9 Hz, 1H), 2.66 – 2.48 (m, 2H), 2.39 – 2.15 (m, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 157.1, 156.6, 141.3, 135.5, 131.7, 130.7, 129.0, 128.8, 127.7, 127.7, 120.3, 120.3, 117.1, 110.8, 110.7, 109.8, 106.5, 55.4, 53.7, 52.7, 39.4; IR (thin film) ν 3342, 3071, 3000, 2933, 1640, 1489, 1462; HRMS (ESI+) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{26}NO_3^+$364.1913; Found 364.1891.

Hydrolysis of Imine 19f: To a stirred solution of imine (*S*)-**19f** (74% *ee*, 43 mg, 96 µmol) in 1:1 THF/H_2O (1.0 mL) at rt was added TFA (0.1 mL) and the resulting solution was stirred vigorously at rt for 3 d and monitored by TLC. Upon completion, volatiles were removed by rotary evaporation and the resulting aqueous solution was diluted with H_2O (3.0 mL). After washing the Et_2O (3 x 2 mL), the aqueous layer was made basic by addition of solid $NaHCO_3$ and then extracted with EtOAc (3 x 2 mL). The combined organic phase was concentrated by rotary evaporation to afford amine **22f** as a yellow oil (16 mg, 72 µmol, 75%): $[\alpha]^{16.7}_D$ -5.67 (*c* 4.6 x 10^{-3}, EtOAc) compared with literature value of $[\alpha]^{23}_D$ -40.1 (*c* 1.16, $CHCl_3$, 98% *ee*).[15]

ASSOCIATED CONTENT

Supporting Information

Linear free energy relationship analyses, NMR spectra for new compounds, and chiral-phase HPLC traces (PDF). This material is available free of charge on the ACS Publications website.

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The authors declare no competing financial interest.

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